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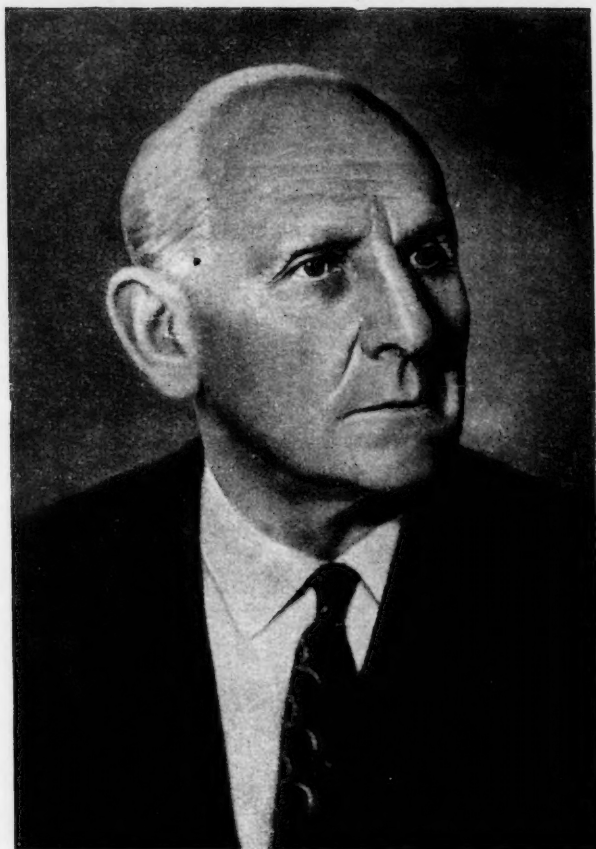
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Sergei Sergeevich Medvedev

DEAR SERGEI SERGEEVICH,

The Presidium of the Academy of Sciences, USSR, Chemical Science Division, and the editorial board of the journal *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, extend you their heartiest congratulations on reaching your seventieth birthday.

You have made an important contribution to the science of chemistry. Your investigations in the field of the oxidation kinetics of hydrocarbons was an important factor in the development of the theory of branched chain reactions and your highly accurate research on polymerization kinetics in the gaseous and liquid phase forms the foundation of this branch of knowledge and has made a permanent contribution to science.

The scientific school established by you has developed the study of polymerization processes and has occupied an important position in world science.

During many years of teaching you have trained a large number of highly qualified chemical specialists who have achieved success in industry and scientific-research institutes.

The Soviet government values your services highly and has awarded you orders, medals, and a Stalin Prize.

Sergei Sergeevich, we wish you health and many years of creative work for the glory of the Fatherland.

Presidium of the Academy of Sciences USSR, Chemical Science Division
of the Academy of Sciences, USSR, and the editorial board of the journal
Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk

INORGANIC AND ANALYTICAL CHEMISTRY

SILICATES OF RARE-EARTH ELEMENTS

COMMUNICATION 4. NEW SILICATES IN THE SYSTEM $\text{La}_2\text{O}_3 - \text{SiO}_2$

N. A. Toropov and I. A. Bondar'

Institute of Silicate Chemistry, Academy of Sciences, USSR

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It was previously reported [1,2] that we first established the existence of the compound $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ in the system $\text{La}_2\text{O}_3 - \text{SiO}_2$ and gave its physicochemical and physical properties. Further investigations of this system showed that two other compounds are formed in it: $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$.

TABLE 1. Results of Annealing and Hardening of the Samples

Composition, wt. %		Residence temp., C.	Residence time	Phase
La_2O_3	SiO_2			
95	5	2200	15 Sec.	Glass
		2100	15 "	"
		2050	30 "	Glass + La_2O_3
		2000	30 "	Glass + La_2O_3
90	10	1775	30 "	$\text{La}_2\text{O}_3 + \text{La}_2\text{O}_3 \cdot \text{SiO}_2$
88	12	2000	30 "	Glass
		1900	30 "	"
80	20	1850	30 "	Glass + $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$
		2100	30 "	Glass *
		2000	30 "	"
		1950	30 "	Glass + $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$
75	25	1850	30 "	Glass + $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2 + \text{La}_2\text{O}_3 \cdot \text{SiO}_2$
		2000	30 "	Glass
		1950	30 "	"
		1900	30 "	Glass + $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$
70	30	1800	30 "	Glass
		1750	30 "	"
		1700	30 "	Glass + $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$
66	34	1700	1 Min	Glass
		1650	1 "	"
		1600	1 "	$\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$
78,3	21,7	1650	15 Hr	$2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$
		1570	15 "	$\text{La}_2\text{O}_3 \cdot \text{SiO}_2 + \text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$

* For the most part, "glass" stands for a mixture of pure glass and fine crystals which separated out during the hardening process.

EXPERIMENTAL

The material and procedure employed, and the results of the investigation were described in previous communications [2-4]. The new variant of the diagram of state is shown in Fig. 1, a,b. As may be seen from Fig. 1, a region of separation within wide limits of temperature and concentration, and three chemical compounds: $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$, $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ and $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ were distinguished in the system. The results of experiments on annealing and hardening are given in Table 1. The temperature and the composition of the invariant points are given in Table 2.

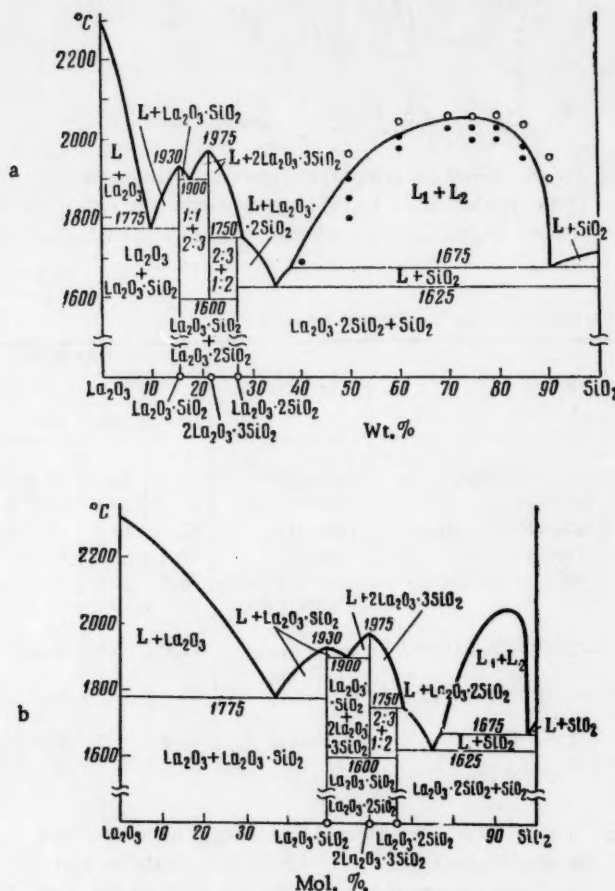


Fig. 1. Diagram of state of the binary system $\text{La}_2\text{O}_3 - \text{SiO}_2$: a) wt. %; b) mol. %.

The compound $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ (1:1) melts without decomposition at $1930 \pm 50^{\circ}$. Fig. 2a shows the x-ray pattern of lanthanum silicate, and Table 3 gives the calculated data of this x-ray pattern. Crystals of this compounds have refractive indices $n_g = 1.875$ and $n_p = 1.855$, a high birefringence ($n_q - n_p$) = 0.020 and are optically biaxial and positive; its sp. gravity $d_{25} = 5.72$. The structural formula of $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ may evidently be represented as corresponding to lanthanum hydroxyorthosilicate $\text{La}_2\text{O}[\text{SiO}_4]$. Fig. 3 shows the primary crystals of lanthanum oxide and the eutectic formed by lanthanum oxide and lanthanum hydroxyorthosilicate.

The compound $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ (2 : 3) was described in detail by the authors in a previous communication [1]. We subsequently established that this lanthanum silicate is stable in the 1600-1975 $^{\circ}$ temperature region. At 1975 $^{\circ}$, $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ melts without decomposition; at 1600 $^{\circ}$ it decomposes into two compounds: $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$ and $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$. Fig. 4 shows individual undecomposed crystals and those which have already decomposed.

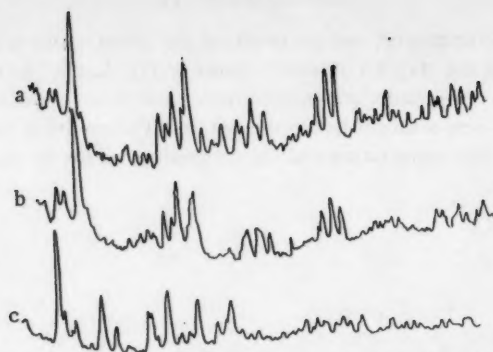


Fig. 2. X-ray pattern of the samples: a) lanthanum hydroxyorthosilicate $\text{La}_2\text{O}[\text{SiO}_4]$; b) lanthanum orthosilicate $\text{La}_4[\text{SiO}_4]_3$; c) lanthanum pyrosilicate $\text{La}_2\text{Si}_2\text{O}_7$.

TABLE 2. Invariant Points in the System $\text{La}_2\text{O}_3 - \text{SiO}_2$

Phase	Process	Composition				Temp., °C.
		Wt. %		Mol. %		
		La ₂ O ₃	SiO ₂	La ₂ O ₃	SiO ₂	
La ₂ O ₃ + La ₂ O ₃ ·SiO ₂ + liquid.	Eutectic	90	10	62,4	37,6	1775
La ₂ O ₃ ·SiO ₂ + liquid	Fusion	84,5	15,5	50	50	1930
La ₂ O ₃ ·SiO ₂ +2La ₂ O ₃ ·3SiO ₂ + liquid	Eutectic	82	18	45,4	54,6	1900
2La ₂ O ₃ ·3SiO ₂ + liquid	Fusion	78,3	21,7	40	60	1975
2La ₂ O ₃ ·3SiO ₂ +La ₂ O ₃ ·SiO ₂ +La ₂ O ₃ ·2SiO ₂	Reaction in the solid state.	78,3	21,7	40	60	1600
La ₂ O ₃ ·2SiO ₂ +2La ₂ O ₃ ·3SiO ₂ + liquid	Incongruent melting	72,0	28,0	32,2	67,8	1750
La ₂ O ₃ ·2SiO ₂ + α-Cristobalite + liquid	Eutectic	65	35	24,7	75,3	1625
α-Cristobalite + L ₁ + L ₂	Liquation	61,8	38,2	23,0	77,0	1675
α-Cristobalite + L ₁ + L ₂	"	10	90	2	98	1675

The refractive indices of $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$, determined by means of high-refractive phosphoric immersion liquids, are $n_o = 1.852$ and $n_e = 1.837$, the birefringence ($n_o - n_e$) = 0.015; its crystals are optically negative and have a hexagonal crystallographic system. The x-ray pattern of $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ is given in Fig. 2, b; Table 3 gives the values of the interplanar spacings and the line strengths of this x-ray pattern.

The compound $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ (1 : 2) melts with decomposition at 1750° , $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ and a liquid being formed. The microphotograph in Fig. 5 shows hexagonal crystals of $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ which have been partially resorbed, and fine plates of $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$, formed during the process of secondary crystallization. $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ crystals are optically positive, with refractive indices $n_g = 1.762$, $n_p = 1.752$, the birefringence ($n_g - n_p$) = 0.010 and the density $d_{25} = 4.85$. In the structural aspect this lanthanum silicate may be described as a pyrosilicate with the composition $\text{La}_2\text{Si}_2\text{O}_7$. Its x-ray pattern is shown in Fig. 2 c, and the calculated data of the pattern are given in Table 3. The eutectic between $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ and SiO_2 may be seen in Fig. 6.

The region of separation is distinguished on the diagram of state of the system by the binodal curve with the critical separation temperature of 2050° and the composition 25 wt. % (6 mol. %) La_2O_3 and 75 wt. % (94 mol. %) SiO_2 . This region is in equilibrium with cristobalite at a temperature of 1675° in the 38.2 - 90 wt. % (77-98 mol. %) SiO_2 concentration range.

TABLE 3. X-ray Investigation of the Compound $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$, $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$, and $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$

$\text{La}_2\text{O}_3 \cdot \text{SiO}_2$		$2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$		$\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$		$\text{La}_2\text{O}_3 \cdot \text{SiO}_2$		$2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$		$\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$	
d/n	I/I ₀	d/	I/I ₀	d/n	I/I ₀	d/n	I/I ₀	d/n	I/I ₀	d/n	I/I ₀
3,25	28	3,68	19	3,38	67	1,039	25	1,575	28	1,655	40
2,85	100	3,37	34	3,25	23	1,027	21	1,526	25	1,608	23
2,33	12	3,24	31	3,14	10			1,487	22	1,579	23
2,18	16	2,95	100	3,06	30			1,369	16	1,542	14
2,04	15	2,85	31	2,88	8			1,349	16	1,515	10
1,99	41	2,37	13	2,83	10			1,331	25	1,455	27
1,95	27	2,24	19	2,66	40			1,315	34	1,420	14
1,894	53	2,18	25	2,49	30			1,289	46	1,384	37
1,811	72	2,13	15	2,38	10			1,268	41	1,376	28
1,739	24	2,02	44	2,17	100			1,217	19	1,343	16
1,581	27	1,96	34	2,11	20			1,191	22	1,323	23
1,572	29	1,935	62	2,04	50			1,168	19	1,276	28
1,512	41	1,883	25	1,931	20			1,158	22	1,256	26
1,465	32	1,853	44	1,878	12			1,144	19	1,231	28
1,275	54	1,821	62	1,826	60			1,077	25	1,165	29
1,231	57	1,814	41	1,712	20			1,058	19	1,127	14
1,071	24	1,591	25	1,675	20			1,045	28	1,104	17
								1,009	25		



Fig. 3. Primary crystals of lanthanum oxide and the eutectic between lanthanum oxide and hydroxyorthosilicate, $\times 240$.



Fig. 4. Decomposition of the compound $\text{La}_4[\text{SiO}_4]_3$ to $\text{La}_2\text{O}[\text{SiO}_4]$ and $\text{La}_2\text{Si}_2\text{O}_7$, $\times 240$.

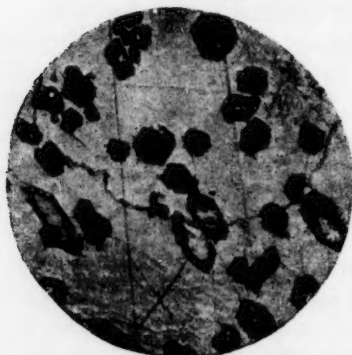


Fig. 5. Resorbed crystals of $\text{La}_4[\text{SiO}_4]_3$ and secondary crystals of $\text{La}_2\text{Si}_2\text{O}_7$, 1800° , $\times 240$.



Fig. 6. Mixture of eutectic composition between $\text{La}_2\text{Si}_2\text{O}_7$ and SiO_2 , $\times 240$.

TABLE 4. Comparison of the Properties of $\text{La}_4[\text{SiO}_4]_3$ and $\alpha\text{-Ca}_2[\text{SiO}_4]$

Compound	Melting point, °C	System and unit-cell parameters	Number of molecules in the unit cell.	Refractive indices	Birefringence	S.G.	Density calculated from x-ray data.	Optical sign	Hardness
$\text{La}_4[\text{SiO}_4]_3$	1975	Hexagonal $a=11,23$ $c=4,674$ $c/a=0,42$	2	$n_o=1,852$ $n_e=1,837$	0,015	5.31 At 25°	5,303	(-)	5-6
$\alpha\text{-Ca}_2[\text{SiO}_4]$	2130	Hexagonal $a=5,45$ $c=7,18$ $c/a=1,31$		Mean $n=1,707$ [8]	Weak [8]	3,07 At 1500°		(+)	5-6

According to Levin and his co-workers [5-7], the limiting composition of separation, i. e. the composition of modifier (MeO)-rich liquid, may be calculated. The authors propose several methods of calculation. Use of the so-called oxygen-volumetric method of calculation requires a knowledge of the ionic radii of oxygen and the metal, the coordination type (A or B) and the mean volume of the area occupied by the oxygen atom in the dense structure. Without giving the intermediate derivations of the formulas or discussing the procedure involved, we will indicate that the values employed for the ionic radii of oxygen and lanthanum were $r_{\text{O}^{2-}}=1,40\text{A}$ and $r_{\text{La}^{3+}}=1,22\text{A}$, respectively, the A type of coordination was adopted and the number of oxygen atoms combined with one cation - the modifier - was $N_0 = 7,61$.

For trivalent cationic-modifiers the calculation was carried out according to the formula

$$\text{R}_2\text{O}_3 \left(\frac{N_0 - 1,5}{2} \right) \text{SiO}_2; \text{La}_2\text{O}_3 \left(\frac{7,61 - 1,5}{2} \right) \text{SiO}_2; \text{La}_2\text{O}_3 \cdot 3,05 \cdot \text{SiO}_2$$

Therefore the calculated limiting separation composition is: La_2O_3 -24,5 mol. %, SiO_2 -75,5 mol. %; the experimentally obtained limiting separation composition is: La_2O_3 -23 mol. %, SiO_2 -77 mol. %. With an La^{3+} ionic radius of 1,04 A, the calculated limiting lamination composition is: La_2O_3 -28,5 mol. %, SiO_2 -71,5 mol. %.

Comparison of lanthanum, calcium and aluminum silicates. On the basis of the analogies between a number of the properties of oxides of rare-earth elements and calcium and aluminum oxides it is of interest to compare the corresponding silicates. From the literature it is known that oxides of rare-earth elements are strong bases, soluble in acids and that they readily form normal salts, even with weak acids. Like Al_2O_3 , the reactivity of these oxides depends on the baking temperature: a high baking temperature makes them inert. However, even after intense baking La_2O_3 does not lose its activity, being similar in this respect to CaO (ease of hydrolysis, carbonization, etc.). Lanthanum silicate, with the general formula La_2SiO_5 (1 : 1), which in the structural aspect is represented by us as the hydroxyorthosilicate $\text{La}_2\text{O}[\text{SiO}_4]$, may be compared with tricalcium silicate Ca_3SiO_5 , on the one hand, and with sillimanite, andalusite and kyanite (disthene), with the general formula Al_2SiO_5 , on the other.

It is known that pure Ca_3SiO_5 , which is monobasic or dibasic with a small angle of the optical axes (2V), a weak birefringence and a negative optical sign, has a truly hexagonal (rhombohedral) symmetry with unit-cell parameters: $a_0 = 7,0\text{A}$; $c_0 = 25,0\text{A}$ at high temperatures. Its pseudostructure is constructed from Ca^{2+} , $[\text{SiO}_4]^{4-}$ and O^{2-} ions, i. e. it belongs to the hydroxyorthosilicates or silicates with an additional oxygen ion, with the structural formula $\text{Ca}_3\text{O}[\text{SiO}_4]$.

The following are characteristic of sillimanite: a rhombic form with unit cell parameters $a_0 = 7,469\text{A}$, $b_0 = 7,653\text{A}$ and $c_0 = 2,876\text{A}$, a marked birefringence (0,02 - 0,023), a positive optical sign and an angle of the optical axes (2V) equal to 25 - 30°. Andalusite also belongs to the rhombic system with an axis ratio $a : b : c = 0,986 : 1 : 0,703$; it separates in the form of tetragonal prisms with a mean birefringence (0,01). Finally, kyanite (disthene) is a triclinic form with a axis ratio $a : b : c = 0,899 : 0,709$; $\alpha = 90^\circ 23'$; $\beta = 10^\circ 18'$; $\gamma = 106^\circ 1'$; polysynthetic twins with a weak birefringence (0,015) are often formed. Comparing data for $\text{Ca}_3\text{O}[\text{SiO}_4]$, $\text{Al}_2\text{O}[\text{SiO}_4]$ with $\text{La}_2\text{O}[\text{SiO}_4]$, it may be assumed that from a number of physical properties of $\text{La}_2\text{O}[\text{SiO}_4]$, such as the high

birefringence, biaxiality and the positive optical sign, this compound has a certain similarity with sillimanite and, possibly, andalusite; in the chemical respect, it evidently behaves like $\text{Ca}_3\text{O}[\text{SiO}_4]$. A comparison of the compound $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$, which we have represented as lanthanum orthosilicate $\text{La}_4[\text{SiO}_4]_3$, with various modifications of calcium orthosilicate $\text{Ca}_2[\text{SiO}_4]$, shows that with regard to a number of properties $\text{La}_4[\text{SiO}_4]_3$ may possibly be nearest to the α -form of $\text{Ca}_2[\text{SiO}_4]$.

Since we have investigated lanthanum orthosilicate in greater detail than the other lanthanum silicates, we give a fuller comparison of the properties of $\text{La}_4[\text{SiO}_4]_3$ and $\alpha\text{-Ca}_2[\text{SiO}_4]$ (Table 4). The other forms of Ca_2SiO_4 characterize the rhombic system (α' - C_2S), the monoclinic (β - C_2S) and rhombic (γ - C_2S) systems.

The investigation of the fine structure of this silicate will make it possible subsequently to draw a complete and accurate analogy with the silicates of other elements. Finally, lanthanum pyrosilicate $\text{La}_2[\text{Si}_2\text{O}_7]$ may be compared with rankinite $\text{Ca}_3[\text{Si}_2\text{O}_7]$. Here, a certain similarity is shown with regard to the nature of melting (both compounds melt with decomposition), the birefringence strength (of the order of 0.01-0.009), and the positive optical sign. Like the $\text{La}_2[\text{Si}_2\text{O}_7]$ obtained by the authors, the native mineral rankinite belongs to the monoclinic system, although synthetic $\text{Ca}_3[\text{Si}_2\text{O}_7]$ is considered to be rhombic.

SUMMARY

1. The diagram of state of the system $\text{La}_2\text{O}_3 - \text{SiO}_2$ was constructed.
2. The three chemical compounds: $\text{La}_2\text{O}_3 \cdot \text{SiO}_2$, $2\text{La}_2\text{O}_3 \cdot 3\text{SiO}_2$ and $\text{La}_2\text{O}_3 \cdot 2\text{SiO}_2$ were synthesized and investigated.
3. The region of separation was established and its limits were determined.
4. An approximate comparison was made between lanthanum silicates and a number of calcium and aluminum silicates.

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INVESTIGATION OF THE STRUCTURE OF THE GALLIUM CHLORIDE COMPLEX WITH THE DYE METHYLENE BLUE

K. A. Bol'shakov, Yu. G. Eremin, and R. P. Evstigneeva

M. V. Lomonosov Institute of Fine Chemical Technology

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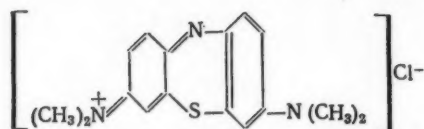
Original article submitted April 12, 1960

The method of infrared spectroscopy is finding wide application in determining the structure of organic compounds. The application of this method in inorganic chemistry up to now has been rather limited, but since organic substances are entering the practice of analytical and inorganic chemistry more and more, the use of infrared spectroscopy is becoming very helpful for inorganic chemists also.

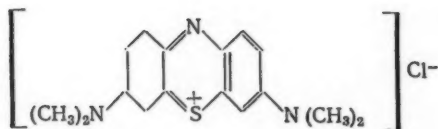
The present work is devoted to a study of the structure of the complex of gallium chloride with the dye methylene blue. Compounds of a similar type, which are termed triple complexes by Babko, are applied mainly in analytical chemistry. Under certain conditions a basic organic dye interacts with a complex anion of a suitable metal, forming a difficultly soluble compound.

Since reactions of metal precipitation by dyes are highly sensitive and selective, and the phenomenon of coprecipitation in general is not characteristic for organic precipitants, the application of these reactions for quantitative analysis is extremely favorable. As far back as 1927, similar reactions were reported for antimony, thallium, gold, and mercury with rhodamines [1]. Methods have been developed for the quantitative determination of zinc and antimony with methyl violet [2]. Babko and co-workers studied the reactions of zinc and cadmium precipitation by various basic dyes [3]. Kuznetsov [4] has performed much fruitful work in this field. However, hitherto there has been no attempt made to study the composition, much less the structure, of complex compounds of this type.

The structures of the original basic dyes in the majority of the cases are controversial, since the location of the positive charge which is inherent in the dye cation is not defined accurately. As Venkataraman [5] indicates, bond hybridization occurs in the molecule of basic dyes, and the positive charge is ascribed to the cation as a whole. In the case of methylene blue, the positive charge may be ascribed either to the sulfur atom or to a nitrogen atom which is connected to methyl groups; for this compound there is possible an ammonium salt



or a sulfonium salt



which differ from each other in the valence states of the nitrogen and sulfur atoms [6]. The ammonium salt is characterized by the presence of pentavalent nitrogen and divalent sulfur, the sulfonium salt by trivalent nitrogen and tetravalent sulfur. Actually the most probable state will be that in which the positive charge belongs to the cation as a whole, i. e., the compound is unsaturated and has conjugated bonds and free electrons.

EXPERIMENTAL

The investigation of the infrared spectra of the gallium chloride complex with methylene blue was carried out on an IKS-II spectrometer with a sodium chloride prism. To eliminate the influence of solvents on the bonds in the complex, the substance was investigated in the solid state. Tablets were pressed (150 atm) from the test material in mixture with potassium bromide, and then placed in the spectrometer. Spectra were obtained for pure anhydrous gallium chloride, methylene blue hydrochloride, and the gallium chloride complex with methylene blue.

The relationships of the transmittance (%) to frequency are shown in Figs. 1, 2 and 3.

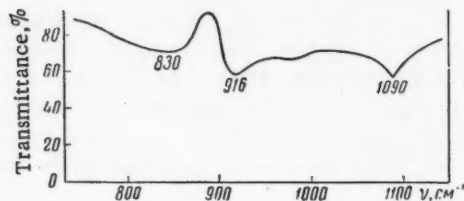
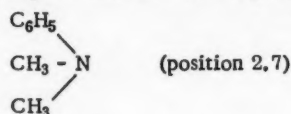


Fig. 1. Infrared spectrum of anhydrous gallium chloride.

From Fig. 1 it is evident that the gallium chloride has absorption bands of moderate intensity at 830, 916, and 1090 cm^{-1} . The spectrum of the methylene blue hydrochloride (Fig. 2, Curve 1) is complex, and the absorption bands of this spectrum require identification on the basis of various reference manuals, of which we made use of the manuals of Bellamy [7], West [8], and Braude and Nachod [9]. The absorption bands at 774 and 802 cm^{-1} are attributed to the nonplanar vibrations of CH, which correspond to the two free hydrogens located on the benzene ring (position 3,4 and 5,6). When there is one free atom of hydrogen on a benzene ring, located between two substituents (position 1 and 8), there are CH absorption bands at 880 cm^{-1} .

The weak absorption bands in the interval 950-100 cm^{-1} correspond to vibrations of trisubstituted derivatives of benzene. The influence of the nature of the substituents on the stability of these bands has been studied very little. The valence vibrations of the C-N bond have an absorption band at 1130, 1250, 1335, and 1350 cm^{-1} . In the present case these absorption bands may be attributed to the groups



The deformation vibrations of the CH_3 groups have an absorption band at 1395 cm^{-1} . The moderate absorption bands at 1430-1450 cm^{-1} may be ascribed to asymmetric deformation vibrations of the CH_3 groups. It should be emphasized particularly that in the methylene blue spectrum there is no absorption band characteristic for the bonds of tetravalent sulfur (1030-1060 cm^{-1} and 1216 cm^{-1}).

Since the system we are studying is conjugated, i. e., it contains both $-\text{C}=\text{C}-$ and $-\text{C}=\text{N}$ bonds, which gave a single absorption band at 1640 cm^{-1} , it does not appear possible to establish strictly to which type of bond this absorption is related. In the spectra we did not cite the absorption for this region, since there the spectra of the dye and the complex are identical.

Proceeding to the analysis of Curve 2, Fig. 2, it should be noted first of all that the shift of the absorption bands in one direction or another (in comparison with their positions in the spectrum of the pure dye) and the appearance of new bands attest to the creation of new bonds in the molecule. A more detailed study of this spectrum and a comparison with the spectra of gallium chloride and of the dye reveals the following: The shift of the absorption bands from 774 and 802 cm^{-1} for the dye to 810 and 830 cm^{-1} for the complex, and the considerable intensifica-

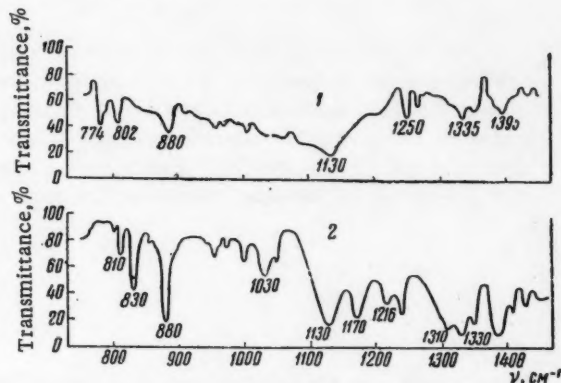


Fig. 2. Infrared spectra of dye and its complex with gallium: 1) Spectrum of methylene blue hydrochloride; 2) spectrum of gallium chloride complex with methylene blue.

tion of the band at 880 cm^{-1} may be caused by an intensification of the deformation vibrations of the CH in the benzene rings which is related to the addition of the anion $[\text{GaCl}_4]^-$ to the molecule. On the other hand, the bonds of the chlorine atom have absorption bands in this region, which is reflected in the spectrum of the gallium chloride (see Fig. 1) and is manifested in the spectrum of the complex, especially at the frequency 830 cm^{-1} .

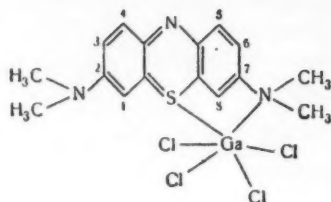
The second very important and essential factor is the appearance in the complex of a strong absorption band at 1030 cm^{-1} and a moderate band at 1216 cm^{-1} . We indicated above that the absence of absorption in these regions of frequency attests to the absence of a tetravalent sulfur atom from the dye molecule, i. e., the positive charge on the dye cation cannot be ascribed to the sulfur atom, just as it probably cannot be ascribed to one of the nitrogen atoms connected with the methyl groups.

The appearance of these absorption bands in the gallium chloride complex with the dye apparently should be attributed to the circumstance that the addition of the large complex anion $[\text{GaCl}_4]^-$ to the dye cation takes place through the sulfur atom, which stabilizes at this atom the position of both the double bond -C=S- and the positive charge of the cation. The appearance of new absorption bands at 1310 and 1170 cm^{-1} and the shift of the band from 1335 cm^{-1} for the dye to 1330 cm^{-1} for the complex are difficult to interpret clearly. In the general case, for nitrogen-containing compounds the absorption bands at $1310\text{--}1330\text{ cm}^{-1}$ refer to the valence vibrations of the bonds



In the present case the appearance of absorption in this region may be caused by an intensification of the valence vibrations of the bonds due to the appearance of an additional coordination bond at the nitrogen. The new strong absorption band at 1170 cm^{-1} probably is attributed to the oscillating vibrations of the CH_3 groups caused by the appearance of still another bond at the nitrogen atom to which these methyl groups are connected.

Thus, the comparative characteristics of the infrared spectra of gallium chloride, the dye methylene blue, and the gallium chloride complex with methylene blue make it possible to draw a preliminary conclusion as to the bonds in the compound which we are studying. The gallium atom has a donor-acceptor bond with the dye molecule through the sulfur atom and a coordinate bond through one of the dimethyl-substituted nitrogen atoms. On the basis of all this discussion, it appears to us that the gallium complex with the methylene blue dye has the following structure:



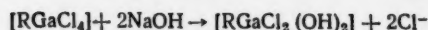
The preference given to the right-hand nitrogen is purely arbitrary, and the coordinate bond of gallium may equally well be effected through the left-hand nitrogen.

The appearance of a new bond in the complex should be reflected also in the structure of the inorganic portion of the molecule. The initial gallium complex is characterized by the following structure: $\text{H}[\text{GaCl}_4]$, i. e., the coordination number of gallium in the given compound is equal to four. The addition of the dye cation to the $[\text{GaCl}_4]^-$ anion gives rise to an increase in the coordination number of the central ion to six, since the dye molecule occupies two coordination sites (one bond of the gallium to the sulfur, the other to the nitrogen). Hence, the complex as a whole is neutral, and the gallium as the central ion holds around itself in the form of addends both the dye molecule and the four atoms of chlorine $[\text{C}_{16}\text{H}_{18}\text{N}_3\text{SGaCl}_4]^0$.

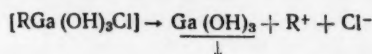
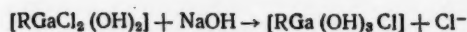
This conclusion agrees well with the data of a potentiometric titration of an aqueous solution of the complex with sodium hydroxide solution. The addition of two equivalents of NaOH does not give rise to a sharp break in pH in the titration, and only the third equivalent of alkali, with the simultaneous appearance of turbidity, gives the

start of a sharp change in pH.

The proposed mechanism of the reaction is as follows: Two OH^- ions enter into the coordination sphere, displacing two chlorine atoms. Since the replacement in the complex of two chlorine ions by two OH^- ions does not entail a change in the charge of the complex, the displaced atoms of chlorine completely lose connection with the complex



where R is the cation of the dye $\text{C}_{16}\text{H}_{18}\text{N}_3\text{S}^+$. The third OH^- ion, displacing from the coordination sphere still another chlorine atom, leads to the complete destruction of the complex, since it creates conditions for precipitation of the gallium



From the structure discussed here, the gallium chloride complex with methylene blue dye can be given the name: chlorogallate of 2,7-bis (dimethylamino) phenothiazine, or tetramethylthionine chlorogallate.

For refinement of the conclusions drawn as to the bonds of gallium to the methylene blue molecule, infrared spectra are presented for the compound of gallium with diethyl dithiocarbamate. Figure 3 shows the infrared spectrum of the initial sodium diethyl dithiocarbamate and of the compound of diethyl dithiocarbamate with gallium. In both cases there is a very strong stable absorption band at 1190 cm^{-1} , caused by the presence in the compound of hexavalent sulfur, which is connected both to the sodium atom and to the gallium atom. The shift of the absorption band from 1130 cm^{-1} for the sodium compound to 1115 cm^{-1} for the gallium compound is obviously explained by the creation of an additional bond of gallium with the nitrogen

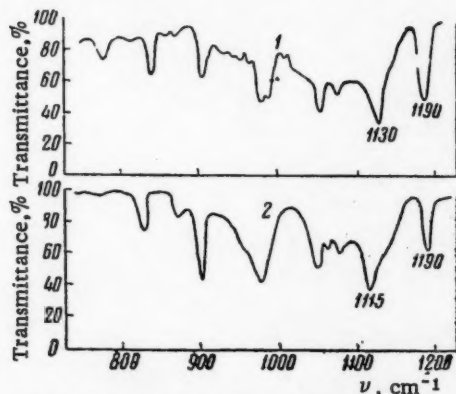
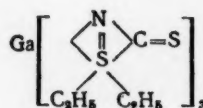
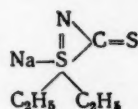


Fig. 3. Infrared spectra of diethyl dithiocarbamate: 1) spectrum of sodium diethyl dithiocarbamate; 2) spectrum of gallium diethyl dithiocarbamate.



The fact that the bonds of the gallium are identical in these two compounds, which contain sulfur and nitrogen atoms, confirms the correctness of the conclusions drawn.

SUMMARY

1. The presence of bonds between gallium and the sulfur and nitrogen atoms has been established in the gallium chloride complex with methylene blue dye. The coordination number of the gallium is equal to 6.

The possibility of the formation of these bonds has been confirmed by a study of the structure of gallium diethyl dithiocarbamate.

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INVESTIGATION ON THE NATURE OF THE MICROPOROUS STRUCTURE IN ACTIVATED CHARCOALS

COMMUNICATION 4. THE GROWTH OF THE MICROPORE VOLUME DURING THE ACTIVATION OF CHARCOALS

M. M. Dubinin

Institute of Physical Chemistry, Academy of Sciences USSR
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Activation of carbonized organic materials by gaseous substances (CO_2 , H_2O), which at sufficiently high temperatures (800-1000°) are oxidizing agents, is the most widely used method for preparing active charcoals. The primary porosity of the carbonization products enables heterogeneous oxidations to take place throughout the entire volume of the charcoal pellets or granules. By preferentially burning away the more reactive constituents of the pellets the porous structure of the charcoal is developed and this gives a considerable increase in adsorptive capacity and specific surface area. The burn-out, that is, that fraction of the original carbonaceous material carbonized up to the activation temperature which is oxidized to gaseous products, is a quantitative measure for the extent of charcoal activation.

Previously [1-5] we have investigated the gradual activation of various carbonized organic materials by carbon dioxide to various degrees of burn-out in the temperature range 750-1000°. The activation was carried out in a rotating cylindrical quartz retort with narrower inlet and outlet tubes and the amount of activating gas passing through the retort per unit time considerably exceeded that of carbon burnt away in the same time. A special arrangement provided an equal distribution of carbon dioxide along the length of the retort [6]. Each charcoal sample prepared is characterized by the activation time t in hours and the fraction ω burnt away. For the activation we used carbonized materials obtained by the thermal decomposition of saccharose (activated charcoals of series A and B), phenol-aldehyde resins (activated charcoals of series C, D and E), wood tar (activated charcoals of series G), wood resin (activated charcoals of series H) and a briquetted mixture of meager mineral coal and wood tar (activated charcoals of series N). For the activation we used the fraction of charcoal granules with 0.5-1 mm particle sizes and also the channel black "Spheron 6" (activated charcoals of series K), which in order to complete the carbonization had been treated thermally under evacuation at a temperature of 950-1000°.

According to experimental data, at a considerable excess of activating gas the burning rate of coal during activation $\frac{dm}{dt}$ is proportional to the amount of charcoal m at the time t

$$-\frac{dm}{dt} = km, \quad (1)$$

hence

$$k = \frac{2,30}{t} \lg \frac{1}{1-\omega} \quad (2)$$

where ω is the weight fraction of the original charcoal burnt away in the time t . Values of the observed kinetic constants k for fractions burnt out lying between 0.02 - 0.05 and 0.60 (0.30 for activated charcoals of the series H), in which range the sizes of the charcoal granules do not change to any considerable extent, are given in Table 1.

The activation energies which characterize the temperature dependence of the kinetic constants have a magnitude typical for chemical reactions.

TABLE 1. Kinetic Constants for the Activation of Charcoals

Series of activated charcoals	Activation temperature °C.	K, 1/hr	Range of ω in which equation (2) is applicable.	Activation energy E, kcal/mole
A	1000	0,12	0,05—0,80	52
B	850	0,010	0,04—0,60	
C	1000	0,14	0,06—0,60	31
D	850	0,019	0,05—0,60	
E	750	0,0095	<0,28—0,60	
G	850	0,056	0,02—0,60	
H	850	0,062	0,02—0,30	
N	950	0,150	0,2 —0,65	

The heterogeneous reaction between the activating gas and charcoal results in burning away carbon throughout the granules and thereby increasing the porosity. According to our investigations, active charcoals are characterized by a polymodular pore-size distribution and they contain various kinds of pores [7]. The sizes of the narrowest pores or micropores are of the same order of magnitude as the size of the adsorbed molecules; the volume of the former is given by the limit volume of the adsorption space W_0 , that is, by one of the constants in the adsorption isotherm equation which we have derived from the theory of the adsorption potential [8-10]. In the wider pores, which are called intermediary pores and have effective radii of sometimes tens of hundreds of Å, at higher pressures capillary condensation occurs. The widest pores, which are called macropores and have effective radii of sometimes a thousand or ten thousand Å, play the role of traffic roads making the inner parts of the charcoal granules easily accessible to the molecules to be adsorbed. Since the specific surface area of the micropores is of the order of 100 m²/g, that of the intermediary pores sometimes ten m²/g, and that of the macropores a few m²/g, the microporous structure of activated charcoals mainly determines adsorption.

According to x-ray data, carbonized organic materials consist mainly of aggregates of graphite-like crystallites the lattice parameters and the sizes of which do not vary much, if the temperature at which the crystallites are formed does not exceed 1000°. In each crystallite the carbon atoms form flat two-dimensional hexagonal lattices, but, unlike graphite crystals, these planar networks are oriented at random with respect to the normal to the basal plane. The free valences of the carbon atoms lying in the prismatic faces of the crystallites are saturated by addition of organic radicals consisting mainly of carbon atoms and connecting atoms in the prismatic faces of adjacent crystallites [11]. This irregularity manifests itself by a background in the x-ray pattern. Of course, the density of the crystallites, as is found from x-ray data, is greater than the mean density of amorphous charcoal and, probably, the latter state is more reactive. The lowering of the mean density may even originate from the presence of closed pores formed by prismatic faces of the crystallites. Since the crystallites themselves and the gaps between them, which are filled up more loosely by irregularly arranged carbon, have dimensions of about the same magnitude as the sizes of the micropores, the formation of a microporous structure may be considered to result from the partial burning away of the more reactive amorphous charcoal or even the crystallites themselves during the activation treatment.

It is convenient to distinguish two stages in the activation process. In the first stage at degrees of burn-out not exceeding $\omega=0.1$ a relatively great micropore volume is formed, probably, because amorphous charcoal is preferentially burnt away and closed micropores are opened. In the second activation stage the formation of micropores mainly results from burning away carbon from crystallites. When assuming such an activation scheme one may derive the relation between the micropore volume and the burn-out of charcoal in the course of the activation and compare the relation found with the experimental data.

Let the active charcoal with the burn-out ω_1 , corresponding to the point where the second activation stage starts, have a limit volume of the adsorption space (micropore volume) equal to W_0^1 . According to the definition, the burn-out is given by

$$\omega_1 = \frac{m_0 - m_1}{m_0}, \quad (3)$$

where m_0 represents the original weight of the charcoal carbonized at the activation temperature and m_1 the weight

of the active charcoal obtained. When the burn-out is raised to the value ω

$$\omega = \frac{m_0 - m}{m_0} \quad (4)$$

the micropore volume is increased and becomes equal to W_0 .

The formation of the micropore volume W_0 corresponds to an amount $m_0 - m$ of carbon burnt away; when referred to a unit mass of active charcoal obtained, this amount is $\frac{m_0 - m}{m}$. The corresponding amount of carbon burnt out at the formation of the micropore volume W_0^1 is equal to $(\frac{m_0 - m_1}{m_1})$. These expressions giving the relative amounts burnt out during activation are analogous to the relative micropore volumes W_0 and W_0^1 , since in the calculation of the micropore volumes formed during activation these volumes are referred to a unit mass of active charcoal obtained, that is, to just m and m_1 .

In the second activation stage the difference

$$\frac{m_0 - m}{m} - \frac{m_0 - m_1}{m_1}$$

may be considered to be the weight of carbon burnt away from crystallites with a density ρ (x-ray).

Then the pore volume formed in the active charcoal, when the burn-out rises from ω to ω_1 , will amount to

$$\frac{1}{\rho} \left[\frac{m_0 - m}{m} - \frac{m_0 - m_1}{m_1} \right],$$

whereas the fraction γ of this volume will correspond to the increase in micropore volume, that is, to the difference $W_0 - W_0^1$

$$W_0 - W_0^1 = \frac{\gamma}{\rho} \left[\frac{m_0 - m}{m} - \frac{m_0 - m_1}{m_1} \right] \quad (5)$$

When replacing m and m_1 in equation (5) by the degrees of burn-out ω and ω_1 from formulas (3) and (4) and defining α by

$$\alpha = \frac{\gamma}{\rho}, \quad (6)$$

we get after some simple algebra that

$$W_0 = W_0^1 + \frac{\alpha}{1 - \omega_1} \left[\frac{\omega - \omega_1}{1 - \omega} \right] \quad (7)$$

For the second activation stage equation (7) gives a linear relation between the micropore volume W_0 and the burn-out function $\frac{\omega - \omega_1}{1 - \omega}$, W_0^1 and

$$\alpha' = \frac{\alpha}{1 - \omega_1} \quad (8)$$

are the parameters of the straight line. For a series of active charcoal samples obtained by activation to various degrees of burn-out starting from the same carbonized material this equation (7) gives a set of straight lines dependent on the values chosen for the parameters W_0^1 and ω_1 ; they are applicable for the second activation stage, that is,

for degrees of burn-out usually lying between 0.1 and 0.5.

When we choose the micropore volume $W_0^1 = V_0$ extrapolated to the burn-out $\omega_1 = 0$ as one of the parameters in equation (7), we get the more simple relation

$$W_0 = V_0 + \alpha \frac{\omega_1}{1 - \omega_1} \quad (9)$$

In this case the parameter V_0 may be considered as the volume of the closed micropores present in the original carbonized material and opened during the activation by a very small and nearly negligible burn-out of carbon.

At various degrees of burn-out for the active charcoal samples obtained from the above mentioned series we have measured the adsorption isotherm of benzene vapor by means of a sorption balance [1-5]. The experimental data are in good agreement with the isotherm equation of the adsorption potential theory for adsorbents of the first structural type [4]

$$a = \frac{W_0}{v} e^{-B \frac{T^2}{\beta^2 (\lg p_s / p)^2}},$$

where a represents the amount adsorbed at the relative pressure p/p_s and the temperature T ; v the volume of a millimole of condensed vapor; B the affinity constant of the characteristic curves, which is equal to 1, when benzene is taken as the standard vapor; W_0 the limit volume of the adsorption space, B the second parameter in the equation, which depends on the size of those micropores which are effective in raising the adsorption potential. Since in activated charcoals of the first structural type the adsorption takes place in the volume of the adsorption space delimited by the walls of the micropores and the fields of the walls at both sides overlap, the limit volumes of the adsorption space W_0 give the micropore volumes of the activated charcoals studied. Therefore, henceforth the values of the constant W_0 will be taken as the micropore volume of the activated charcoals.

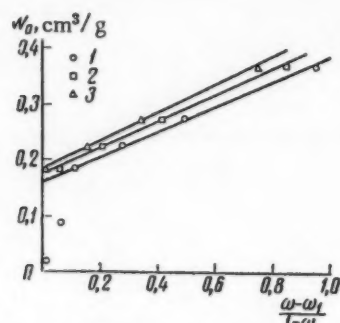


Fig. 1. Micropore volume as a function of burn-out for activated charcoals of series C when the linearized equation (9) is used: 1) $\omega_1 = 0$; 2) $\omega_1 = 0.050$; 3) $\omega_1 = 0.100$

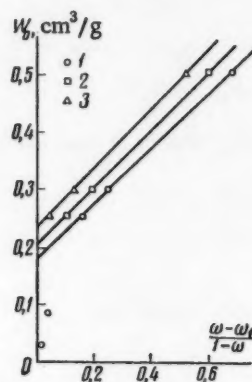


Fig. 2. Micropore volume as a function of burn-out for activated charcoals of series D when the linearized equation (9) is used: 1) $\omega_1 = 0$; 2) $\omega_1 = 0.050$; 3) $\omega_1 = 0.100$

As typical examples, in Figs. 1 and 2 we have plotted, according to the linearized equation (9), the micropore volume as a function of burn-out for activated charcoals of series C and D at various values of the parameter W_0^1 corresponding to degrees of burn-out ω equal to 0, 0.05 and 0.100. In the plots for the second stage of the activation

TABLE 2. The Constants of Equation (9) Calculated from the Parameters of the Straight Lines.

Series of activated charcoals	ω_1	$W_0, \text{cm}^3/\text{g}$	$\alpha', \text{cm}^3/\text{g}$	$V_0, \text{cm}^3/\text{g}$ from (11)	$\alpha, \text{cm}^3/\text{g}$ from (12)
C	0	0,162	0,213	0,162	0,213
	0,050	0,175	0,225	0,164	0,214
	0,100	0,187	0,236	0,163	0,212
D	0	0,177	0,482	0,177	0,482
	0,050	0,202	0,510	0,177	0,485
	0,100	0,232	0,530	0,178	0,478

the experimental points are described quite satisfactorily by straight lines.

According to equations (7) and (9), at $\omega = 0$

$$V_0 = W_0^1 - \frac{\alpha}{1 - \omega_1} \cdot \omega_1 \quad (11)$$

and from relation (8)

$$\alpha = \alpha' (1 - \omega_1) \quad (12)$$

The straight line parameters W_0^1 and α' found from the plots in Figs 1 and 2 and the values of V_0 calculated from them by means of relation (11) and those of α derived from formula (12), that is, the constants of equation (9), are given in Table 2.

According to the data of Table 2, for each series of activated charcoal prepared from phenol-aldehyde resin the parameters V_0 and α are found to have practically constant values. In spite of the fact that the α values for series C differ considerably from those for series D, the V_0 values, which are assumed to be the volumes of the closed micropores in the carbonized material used for preparing both the charcoals of series C and those of series D, are practically equal (0.16-0.18 cm^3/g).

In Table 3 are assembled the values of the constants found by applying equation (9) to all series of activated charcoals investigated in the ranges of burn-out where the experimental data are described by the said equation. In order to estimate the γ values we used the x-ray density found for the crystallites in the activated charcoals from phenol-aldehyde resin [12].

TABLE 3. Constants Found by Applying Equation (9) to the Second Activation Stage of the Various Charcoal Series.

Series of activated charcoals	Activation temperature, °C	$V_0, \text{cm}^3/\text{g}$	$\alpha, \text{cm}^3/\text{g}$	Suitable range of ω	$\gamma = 1,91\alpha$
A	1000	0,15	0,54	0,2—0,4	~1
B	850	0,15	0,57	0,1—0,45	~1
C	1000	0,16	0,21	0,1—0,5	0,41
D	850	0,18	0,48	0,1—0,45	0,94
E	750	0,15	0,24	up to 0,45	0,45
G	850	0,070	0,35	0,1—0,35	0,66
H	850	0,065	0,23	0,1—0,5	0,43
K	950	0,035	0,42	0,1—0,55	0,80
N	950	0,13	0,37	up to 0,50	0,70

Under the activation conditions for the charcoals of the series A, B, and D in the second stage mainly micropores are formed as a result of burning away carbon crystallites. In the case of the activated charcoals of the other series the burn-out only partly leads to growth of the microporous structure. When applying an equation of the type (9) to the total pore volume of activated charcoals of series N we found $\gamma=0.95$, that is, a value practically equal to one.

For the activated charcoals of the series C, D and E prepared from phenol-aldehyde resin it follows by comparing the kinetic constants k for burning away during activation (Table 1) with the values of α (Table 3) that too high and too small burning rates are unfavorable for the development of a microporous structure in an activated charcoal. The volumes of the closed pores present in the original carbonized materials depend on the origin of the latter and they vary to a considerable extent from 0.17 for the carbonized phenol-aldehyde resin to 0.03 for the channel black; they embrace 40-10% of the micropore volume for the charcoal samples corresponding to activation by burn-out up to $\omega=0.5$.

CONCLUSIONS

1. Previously obtained experimental data on the growth of the micropore volume in active charcoals in the course of an activation by means of carbon dioxide have been analyzed in more detail as a function of the fraction burnt away at various temperatures and this has been done for several carbonized organic materials.
2. In the first activation stage the micropore volume grows mainly because the closed pores occurring in the carbonized organic materials from which we started are opened. In the second activation stage micropores are formed chiefly by burning away cristallites from the charcoal.
3. We have derived an equation which expresses the micropore volume as a function of burn-out and this is in good agreement with experimental data for the second activation stage.
4. We have noted which role the activation kinetics have in the growth of the microporous structure in active charcoals.

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STUDY OF CAPILLARY CONDENSATION IN HIGHLY DISPERSE SYSTEMS

COMMUNICATION 4. CAPILLARY CONDENSATION IN SYSTEMS COMPRISING A GREAT NUMBER OF CONTACTING PARTICLES.

L. V. Radushkevich

Institute of Physical Chemistry, Academy of Sciences USSR

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In previous communications [1-3] we have given a theoretical calculation of capillary condensation around the point where two spheres of equal or different radii make contact. This condensation can also take place in systems comprising a great number of contacting particles. Various loose materials, powders, dust sediments, several adsorbents (carbon black, silicagel), and aggregates of a great number of particles in aerosols belong to this type of system. When such substances are exposed to vapors of any liquid, for instance, to water vapor, then vapor may condense around the points of contact between the particles, because over the curved meniscus of the previously condensed liquid the vapor pressure is lowered. Approximate calculations for packings of equal spheres have been put forward by many authors, but in its most general form the problem has not yet been discussed, although the widely spread occurrence of the said systems would deserve such a discussion. Here we will show that the calculations come to an application of very general relations, which may be used not only for packings of ideal spheres, but also to particles of an intricate shape and to various kinds of contacts, while the dimensionless functions of the relative vapor pressure and particle sizes, as we have introduced, play the predominant role.

If the system comprises a great number of particles, in a discussion of capillary condensation the following complications must be taken into account: 1) since each particle of the system touches several other particles and in the general case the number of contact points varies from particle to particle, for a calculation of the capillary condensed volumes one must have information on the statistical distribution of the various kinds of contacts in the system; 2) in polydisperse systems one must take into account the particle size distribution, since the amount of condensed liquid depends upon this distribution; 3) when the vapor pressure is raised, the separate liquid menisci at adjacent contact points may coalesce and, later on, the spaces between the most densely packed particles may even fill up completely; in this stage the process differs from capillary condensation in the regions in the direct vicinity of the contact points; 4) when describing the overall sorption in particle packings, besides capillary condensation, vapor adsorption on that part of the particle surface which is not blocked by capillary condensed liquid must be taken into account, whereas in this, one must pay attention to the gradual diminution of this surface area resulting from capillary condensation.

At present we do not dispose as yet of those data on the structure of actual particle packings which are required to describe capillary condensation in such systems in its general form. Previously [4] it has been described for a few simpler cases how the condensation proceeds after the menisci have coalesced and we will not dwell longer on it. In the present paper we will give calculations for systems comprising contacting ideal spheres and for packings of particles with an irregular shape.

Smooth spherical particles. Let the system comprise a great number N of mutually touching spheres with radii $R_1, R_2, \dots, R_i, \dots$, whereas the fraction of the number of spheres with radius R_i in the packing is taken to be

$$\varphi(R_i) = N_i/N.$$

Evidently, the total volume of the spheres in the packing is

$$W = \frac{4}{3}\pi \sum_i N_i R_i^3 = \frac{4}{3}\pi N \sum_i \varphi(R_i) \cdot R_i^3.$$

The mathematical expectation for the third power of the sphere is given by

$$\bar{R}^3 = \sum_i \varphi(R_i) \cdot R_i^3,$$

and this relation represents the mean value because here the normalization condition $\sum_i \varphi(R_i) = 1$ is satisfied. Consequently,

$$W = 4/3\pi N \cdot \bar{R}^3.$$

As a result of capillary condensation a ring of liquid is formed around each point of contact. The volume v_{ih} of each of these rings depends on the radii R_i and R_h of the pair of touching spheres. If the total number of contacts in the system is equal to \underline{n} , and n_{ik} of them correspond to pairs with radii R_i and R_k , then

$$\psi(R_i, R_k) = n_{ik}/n,$$

and therefore,

$$\sum_i \psi(R_i, R_k) = 1$$

The total volume of condensed liquid in the entire packing of N spheres is equal to

$$V = \sum_i \sum_k n_{ik} v_{ik} = n \sum_i \sum_k \psi(R_i, R_k) v_{ik}.$$

The volume of liquid around the contact point between two spherical particles with radii R_i and R_k is given by the relation which we have derived previously [3]:

$$v_{ik} = 1/3\pi R_i^3 U_{ik},$$

where $R_i \leq R_k$, whereas U_{ik} represents a dimensionless function of the ratio R_k/R_i and the Kelvin radius $C=2\sigma v_0 (RT \ln p_s/p)^{-1}$. We have given tables of the function U_{ik} . In this way

$$V = n \sum_i \sum_k \psi_{ik} v_{ik} = 1/3\pi n \sum_i \sum_k \psi_{ik} R_i^3 U_{ik}.$$

If \underline{i} lies between 1 and \underline{l} , then the number of terms in this sum is equal to $\underline{l}(\underline{l} + \underline{i})/2$.

The specific volume of the liquid in the entire packing is equal to

$$\omega = V/W = 1/4\pi \sum_i \sum_k \psi_{ik} R_i^3 / \bar{R}^3 U_{ik}. \quad (1)$$

Here $\nu = \underline{n}/N$, that is, the mean number of contacts per sphere in the packing. Evidently, ν is equal to half the so-called mean coordination number ν_0 , that is, $\nu = \nu_0/2$, since each ring of liquid is common to two spheres.

Usually, the amount sorbed is expressed as grams (or moles) sorbate per gram sorbent, therefore,

$$a_k = 1/4 \nu \cdot \rho_L / \rho_p \sum_i \sum_k \Psi_{ik} R_i^3 / \bar{R}^3 U_{ik} \frac{g_i}{g^*}, \quad (2)$$

where ρ_L is the density of the liquid and ρ_p the density of the nonporous particles.

The derived formulas (1) and (2) are of general validity, since they are applicable to any (regular or irregular) packing of ideal spheres at a given size distribution. Both relations are simplified considerably, when one goes over to mean values. The mathematical expectation of $R_i^3 U_{ik}$ may be represented as

$$M = \sum_i \sum_k \Psi_{ik} R_i^3 U_{ik} = \bar{R}^3 \bar{U} = \bar{R}^3 \cdot \bar{U}.$$

Therefore, (1) is transformed to

$$v = 1/4 \nu \bar{U}, \quad (3)$$

and also from (2) we get

$$a_k = 1/4 \nu \rho_L / \rho_p \bar{U}. \quad (4)$$

Hence it follows that in order to calculate a_k it suffices to find the mean value \bar{U} at given sphere radius distributions φ_i and contact distribution Ψ_{ik} for each system of spherical particle packings. We note that the distribution of the number of contacts, in its turn, is a function of the sphere size distribution. From formula (2) (or from (4)) we get for the particular case of a monodisperse system where $\bar{U} = U_{11}$:

$$a_k = 1/4 \nu \rho_L / \rho_p U_{11}, \quad (5)$$

where the function U_{11} corresponds to the touching of spheres with equal radii. For this simplest system ν can be determined empirically [5] and, thanks to this, at given ρ_L and ρ_p one may easily calculate a_k at various ρ / ρ_s , if one uses the tabulated values of the function U_{11} . In this way the capillary condensation isotherm can be constructed. Examples of these isotherms are shown in Fig. 1.

Packings of regular spheres are discussed in detail in many papers [6] and they are realized experimentally by using macroscopic, smooth spheres. These packings are encountered in several sorbents with a clearly developed globular particle structure. However, systems comprising touching particles of more or less irregular shapes are more widely spread. For such systems one may only give an approximate calculation.

Irregularly shaped particles. Although for systems comprising touching solid particles with an irregular shape it is impossible to give an exact calculation of capillary condensation, for all that we get an accurate and quite sufficient approximation, if we confine ourselves to particles of a not very intricate shape and use the data found above for ideal spherical particles.

The point in the calculation method given below consists in the fact that in capillary condensation occurring near the point of contact between two particles an intricate shape of each of them generally has no direct influence on the course of the process. So, if two irregular particles have small spherical regions in their surfaces along which these particles touch, then the calculation in principle is analogous to that which we have given for ideal spherical particles. By inscribing spheres as accurately as possible in the said region of the particles, that is, in the regions adjacent to the point of contact, we will obtain for a pair of irregularly shaped particles just the same results as we got for two touching spheres of similar radii. The relative "protuberance height" or the surface roughness sets a restriction to this result. In the paper [1] it has been shown that the height x_M of the spherical segment cut by

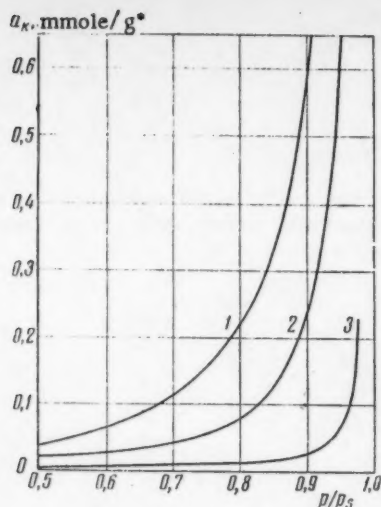


Fig. 1. Capillary condensation isotherms of C_6H_6 vapor for typical carbon black samples at $\nu=8$; $\rho_L=0.879$ g/cm³, $\rho_P=1.8$ g/cm³, as calculated from equation (5) for: 1) $R=500$ Å; 2) $R=1000$ Å; 3) $R=5000$ Å.

the contour of the liquid meniscus on the particle at $p/p_s = 1$ is equal to $x_M=0.436$ for two particles with equal radii. This height $x_M=h$ determines the extreme position of the meniscus when capillary condensation takes place entirely according to the mechanism described previously, that is, when the spherical sections of the rough particles are analogous to whole spheres. If the radius of curvature for the roughness amounts to the fraction R/A of the radius A of the entire particle, then at $h/A=0.436$ R/A the process will proceed according to the said mechanism; if h/A is smaller than this value, the course of filling will go otherwise. Let us assume, for instance, that $R=0.1$ Å; then $h/A=0.0436$. Consequently, in this case the admissible height of roughness should not be smaller than $\sim 4\%$ of the particle radius.

On the surface of an irregularly shaped particle one may delimit several regions which may be assumed to be spherical segments with various curvatures. Practically any touching between irregular particles may be reduced in this way to touching of spherical regions on their surfaces. For a further discussion a certain characterization of the sizes of irregularly shaped particles is necessary. It is most expedient to use the concept of the weight radius A , which is defined as the radius of the sphere with the same mass as that of the irregularly shaped particle. In this way $\underline{m} = \frac{4}{3}\pi A^3 \rho_P$ where \underline{m} represents the mass of the particle.

The radii R_i of the spherical regions in the particle surface may be either greater or smaller than the weight radius introduced here. The case where $R_i \gg A$ is seldom found on the surface of an irregularly shaped particle,

since, otherwise, these regions would have a mean size greater than A , which is nonsense. The problem under consideration most likely corresponds to the case where $R_i \leq A$. Consequently, we are dealing with particles with "irregularities" or with "angular" or "rough" particles; on them, besides places with a positive curvature, there may even exist regions where the curvature is negative (depressions etc.) and where during condensation of vapor "cup-shaped" menisci may even be formed independent of the capillary condensation near the points of contact. As yet we will not take into account this effect, but an estimate shows that it is relatively small.

The amount sorbed by the capillary condensation around the points of contact between irregularly shaped particles can be found by a method completely analogous to that used for smooth spheres and thus, as would be expected, one obtains relations similar to the previous ones. Let the packing comprise N irregularly shaped particles with weight radii $A_1, A_2, \dots, A_i, \dots$. Similarly as we found previously, the volume of the entire packing is equal to

$$W = \frac{4}{3}\pi N \bar{A}^3,$$

where

$$\bar{A}^3 = \sum_i \varphi_i(A_i) A_i^3.$$

The volumes of liquid around the points of contact with the radii $R_1, R_2, \dots, R_i, \dots$, just as previously, are equal to

$$v_{ik} = \frac{1}{3} \pi R_i^3 U_{ik},$$

and the total volume of liquid in the system is

$$V = \sum_i \sum_k n_{ik} v_{ik} = \frac{1}{3} \pi n \sum_i \sum_k \zeta_{ik} R_i^3 U_{ik};$$

The relative liquid volume in the packing amounts to

$$\omega = V/W = \frac{1}{4} n \sum_i \sum_k \zeta_{ik} R_i^3 / \bar{A}^3 U_{ik}.$$

Here $\zeta_{ik} = n_{ik}/n$ characterizes the distribution of the number of contacts between irregularities of the type (i,k), since $\sum_i \sum_k \zeta_{ik} = 1$.*

In analogy to the procedure above we introduce the mathematical expectation

$$M = \sum_i \sum_k \zeta_{ik} R_i^3 U_{ik} = \bar{R}^3 \cdot \bar{U},$$

and then

$$\omega = 1/4 v \bar{R}^3 / \bar{A}^3 \bar{U} = 1/4 v \bar{\chi}^3 \cdot \bar{U},$$

where is defined

$$\bar{\chi}^3 = \bar{R}^3 / \bar{A}^3.$$

Correspondingly, the amount sorbed in the system is now found to be

$$a_h = 1/4 v \bar{\chi}^3 \cdot \bar{U}. \quad (6)$$

Since under our assumption on the character of the irregularities on the particles it may be supposed that generally all R_i are smaller than the weight radii A_i , the mean ratio $\bar{\chi}^3$ is smaller than one. Therefore, by comparing (6) and (4) we find that, in systems of irregularly shaped particles, sorption by capillary condensation generally tends to be lowered. It is not difficult to draw more definite conclusions by comparing monodisperse systems of irregular particles with monodisperse systems of spherical particles.

If in a system of irregular particles all weight radii A_i are identical and equal to A and the particles themselves have a homogeneous roughness, that is, all R_i are identical and equal to R , then

$$\chi = R/A,$$

and hence

$$a_h' = 1/4 \rho_L / \rho_p \cdot v' \chi^3 U_{11}, \quad (7)$$

where U_{11} depends only on R .

The latter case can be most easily compared with data on packings of ideal smooth spheres of the same material for sorption of one and the same vapor. If smooth spheres of equal size touch, the amount sorbed is given by relation (5). We note that U_{11} in the formulas (5) and (7) are different, since in the first of them U_{11} depends on the sphere radius A , whereas in the second it depends on the radius of the irregularity, that is, on R . Therefore, we write in (5): $U_{11} = U(A)$ and in (7): $U_{11} = U(R)$, so that:

$$a_h' / a_h = \chi^3 \frac{U(R)}{U(A)} \cdot v' / v.$$

For the comparison here it is inevitable to take $v' = v$, since the irregular particles and the spherical ones must be compared in identical packings (although generally v is somewhat smaller than v'). We take one contact per irregularity, but per irregular particle one has to take v' contacts, which corresponds to v contacts on one ideal sphere. Consequently,

$$a_h' / a_h = \chi^3 \frac{U(R)}{U(A)}. \quad (8)$$

* Thus even the cases where an irregularity of one particle touches two or more irregularities of another one are automatically taken into account.

As we have shown previously [1], at $p/p_s = 1$, U takes one and the same value for a given substance, independent of the particle size. Therefore, for $p/p_s = 1$ we have $U_\infty(R) = U_\infty(A)$ and then

$$a'_h/a_h = \chi^3. \quad (9)$$

Since χ is smaller than one, it follows that $a'_k \ll a_k$. If $p/p_s < 1$, it has to be taken into account that U depends on the particle radius. In the paper [1] it has been shown that U decreases, when the sphere radius is raised. At $R < A$ it follows that $U(R) > U(A)$. But χ^3 depends more strongly on the radius than does U . For instance, for C_6H_6 we find from Table 3 of the paper [1] at $p/p_s = 0.9$ for $R = 1 \cdot 10^{-6}$ cm, $U = 12.4\%$ and for $A = 1 \cdot 10^{-5}$ cm, $U = 0.99\%$, whereas $\chi = 0.1$. Hence $a'_k/a_k = 0.0124$. Thus, if the irregularities on the particle have radii ten times smaller than the weight radius, the effect of capillary condensation is lowered considerably with respect to that for smooth particles. It may be shown generally that the function $f(R) = R^3 U(R)$ increases slowly at raised R and, consequently always $a'_k < a_k$; hence one finds that for rough particles at all p/p_s the capillary condensation is lowered, if one refers the amount of liquid condensed to a unit volume (or mass) of packing. This general result leads to the conclusion that among packings of particles of a ground material one should also encounter such samples of packing for which the contribution of capillary condensation to the total amount of adsorbed vapor is negligibly small. Smooth particles or those having irregularities with a curvature almost equal to the curvature of the particle, when packed, should give a greater capillary condensation than do particles with small irregularities (roughnesses). The comparison which we have made between systems of particles with various roughnesses makes it noteworthy to disentangle the contribution of proper adsorption and capillary condensation before one goes over to conclusions on the course of the overall sorption process in systems of touching particles.

CONCLUSIONS

1. For the description of capillary condensation in systems comprising a great number of touching particles it is necessary to have in mind three kinds of statistical distributions: a) the particle size distribution; b) the distribution of the number of contacts per particle; c) the size distribution of the irregularities on the surface of rough particles.
2. General equations for the capillary condensation isotherm in various systems of touching particles have been derived for the special case where the menisci around the contacts are still isolated from each other.
3. A method enabling one to calculate capillary condensation in systems of irregularly shaped particles has been worked out and it has been found that in such systems the amount sorbed may be considerably smaller than in similar systems of smooth spheres.

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* The values of U in the table of paper [1] are half those of U_{11} , because there the formula for v was given with the coefficient $2/3$ and not with $1/3$, as was used in the subsequent communications, but this does not change the conclusion drawn above.

THE FORMATION OF CARBON DENDRITES IN THE DECOMPOSITION OF ALCOHOLS ON NICKEL

A. A. Balandin, A. P. Rudenko and G. Stegner

M. V. Lomonosov Moscow State University

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The fact that in the first stages of carbon deposition in the catalytic conversion of organic substances the activity of the catalysts is preserved or even increased suggested the idea that the carbon deposits formed have a dendritic structure. According to the "dendrite hypothesis" of Balandin and Kotelnikov [1-3], carbon deposits on catalysts do not form a continuous film but form dendrites, which only partly cover the surface so that in the initial stages of carbon deposition the reacting substances have access to the catalyst surface "similarly as rain gets to the ground in a wood". It has been attempted to observe directly by means of a microscope the carbon dendrites formed [4,5]. Actually, Radushkevich and Luk'yanovich made the first direct observation of carbon dendrites under an electron microscope [6]. These authors studied carbon deposits formed in the decomposition of carbon monoxide on iron. It is true that they themselves did not draw conclusions on the dendritic structure of the carbon formations which they observed. The carbon fibers which several authors have found in the thermal decomposition of hydrocarbons or in the decomposition of carbon monoxide on metals [7-10] are nearly alike to dendrites as regards their structure and genesis.

In the present study when investigating the carbonaceous substance obtained by decomposing alcohols on nickel sheets we succeeded in observing carbon dendrites under an electron microscope; their dendritic structure and growth in the form of screw dislocations cannot be doubted. The carbon dendrites which we have observed in several details recall the formations described by Radushkevich and Luk'yanovich [6], but they have a better developed dendritic structure. Besides stratified and ramified dendrites, we also found carbon fibers similar to those described previously [7-10], being of uniform thickness along their entire length and having a much smaller diameter than that of the sheet-like and branched dendrites. Moreover, in the carbonaceous substance we have detected metallic nickel in the form of formations giving the kind of x-ray lines characteristic for large crystals. In our opinion, these formations are dendrites of hexagonal nickel, since one of their lattice parameters is close to the corresponding value for the graphite lattice. In this investigation we tried to ascertain the growth mechanism of the carbon dendrites and the nature of the active centers at which carbon is deposited. The points where the screw dislocations enter the surface of the nickel single crystals were assumed to be the active centers.

EXPERIMENTAL

We have investigated the formation of carbonaceous material on nickel sheets kept in the quartz reactor of a flow system [11] during the catalytic decomposition of ethyl alcohol, *n*-hexyl alcohol or cyclohexanol in the temperature range 400-800° at atmospheric pressure. The experimental procedure was analogous to that described previously [12]. In the reactor were placed two nickel sheets 100 × 9 mm with a thickness of 0.3 mm and their surfaces were treated in the way indicated below. New sheets were taken for each experiment. The reacting substances were fed at a rate 9 ml/hr. The amount of carbonaceous substance formed was calculated from the weight increase of the nickel sheet. We have carried out microscopic investigations of the carbon deposits formed on nickel sheets and in the various stages of the deposition; we did this by means of the light microscopes MIN-4 and MIM-6 at magnifications 37-260 and an electron microscope at magnifications 2000-1570. We analyzed the carbonaceous substance chemically and tested it magnetically and by means of x-rays.

Since preliminary experiments have shown that on nickel sheets polished by treating with a mixture of 3 parts nitric, 1 part sulfuric, 1 part phosphoric and 5 parts acetic acid no deposition of carbon occurs, according to [13], and on sheets etched until the mosaic structure of the metal is visible (Fig. 1,a) by the procedure of [14] by means of a mixture of 2.5 parts acetic, 5 parts nitric acid and 2.5 parts water the deposition of carbon proceeds easily, we

did all experiments on etched sheets.

As follows from Table 1, the change in rate of carbon deposition at increasing decomposition temperature has the same general character for all alcohols studied. At 400° the rates are very small; when the temperature is raised to 600°, they increase sharply; when the temperature is raised further, they decrease. Above 600° one begins to observe the formation of carbon films on the walls of the reactor and the catalyst tube and meanwhile also a great amount of tar-like products is given off. In most cases the rate of carbon deposition attains a maximum in 2-3 hours, that is, the carbon which in the first 2-3 hours is deposited enhances the catalytic activity for the deposition of carbon. For all three alcohols studied it is found that the formation rates of the carbonaceous substance are proportional to those of the gaseous products and inversely proportional to the aldehyde (ketone) content in the reaction product (Tables 1-3).

TABLE 1. The Way in which the Rate of Carbon Deposition on Nickel Sheets, when Expressed in Grams Carbon per Hour, Changes in the Course of Time

Alcohol fed	Temperature °C	Time, hours					
		1	2	3	4	5	6
Ethyl alcohol	445	0,0367	0,0666	0,0606	0,0653		
	600	0,5697	0,6625	0,5783			
	800	0,0169	0,0161				
n-Hexyl alcohol	445	0,0218	0,0210	0,0272	0,0382	0,0848	0,0864
	535	0,1237	0,4005	0,4284			
	600	0,6494	0,0463	0,0505	0,0120		
	800	0,0342	0,0350				
Cyclohexanol	605	0,1375	0,6650	0,0540			
	820	0,0655	0,0593				

TABLE 2. The Way in which the Rate of Aldehyde Formation on Nickel Sheets, when Expressed in Grams Aldehyde per Hour, Changes in the Course of Time.

Alcohol fed	Temperature °C	Time, hours					
		1	2	3	4	5	6
Ethyl alcohol	445	0,0970	0,0440	0,0360	0,0350		
	600	0,0515	0,0202	0,0372			
	800	0,0000	0,0000	0,0000			
n-Hexyl alcohol	445	—	0,1602	0,0950	0,1010	0,0960	0,0900
	600	0,0875	0,2040	0,1860	0,1910		
	800	0,0000	0,0000	0,0000			

Simultaneously with the changed formation rate of carbon during the accumulation of the carbonaceous substance on the nickel sheets it is found that the composition of the gaseous and liquid decomposition products has altered (Tables 1-3); this indicates that the decomposition of the substances fed changes somewhat under the influence of the carbon formed. However, in its general pattern the character and the mechanism of carbon formation in the cases discussed are similar to those which we have observed in the decomposition of these alcohols on a copper-silicagel catalyst [12,15].

In the initial stage of carbon deposition on the nickel sheets (1-2 min after the start of the experiment) the surface is only found to get yellow, then the carbonaceous film turns brown, darkens and gets the appearance of a very loose velvet-black mass, which can be easily stripped from the sheet. Elementary analyses of the carbonaceous substance have shown (Table 4) that its carbon content rises when the temperature is raised. By studying

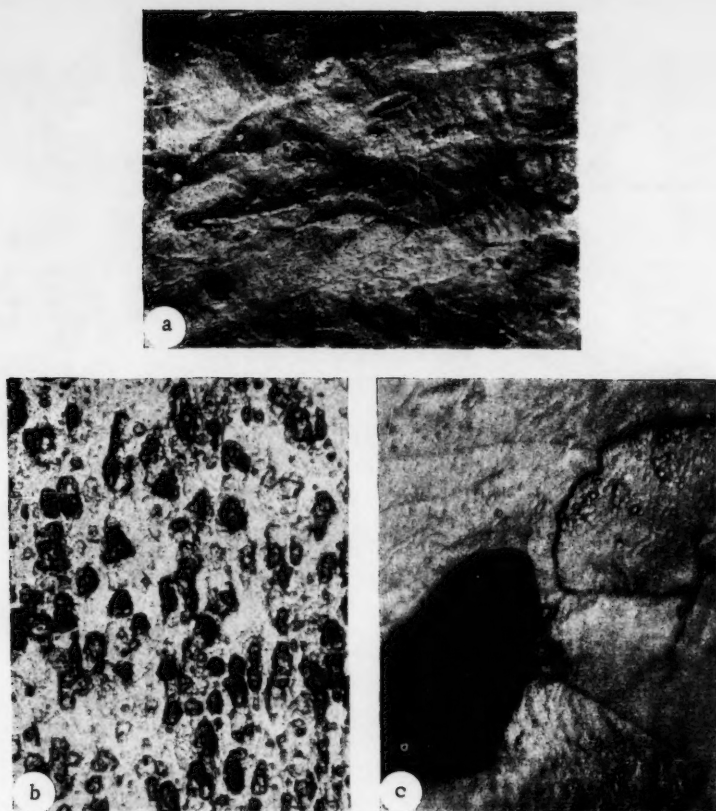


Fig. 1. Microphotographs of nickel sheets under a MIM-6 microscope: a) before the experiments; magnification 136x; b and c) after an experiment with cyclohexanol at 600°; magnification 58x (b); 260x (c).

the carbon films deposited in the initial stage under a microscope it has been shown that the carbonaceous deposit does not at all appear as a film but it looks like islets and stains adapted to several details of the nickel microstructure (microcrystal grains). But not all visible and externally identical grains are found to be covered by carbon. Besides intensively darkened grains having their entire surface covered with the carbonaceous deposit, one often encounters grains quite free of carbon or only partly covered by it (Fig. 1, b and c). When the nickel sheets are covered to a greater extent, the carbonaceous deposits take possession of all grains; the layer of carbon acquires an appreciable thickness and expands in the form of a porous loose mass. No differences at all were noted in the exterior appearance of the carbonaceous deposits, when one of the above mentioned alcohols was replaced by another of these. Electron microscope photographs of the carbonaceous substance taken at high magnifications and showing the dendritic structure are given in Fig. 2.

All carbon deposits obtained contain metallic nickel. As the temperature at which they are obtained is raised, their nickel content varies in the following way

450-460°	3.3-3.5%
600°	5.8-6.1%
800°	1.5-1.8%

that is, there exists a relation between the rate of carbon deposition and the nickel content in the carbonaceous substance obtained. Nickel is also found* in the carbon deposits on the reactor walls and in the tar-like products condensed on the walls of the cold part of the catalyst tube. By x-ray diffraction where the lines characteristic for nickel were found to be present, by the magnetic properties of the carbonaceous substance studied and from its

*Nickel was determined colorimetrically by the color reaction with dimethylglyoxime in an ash probe obtained by burning a weighed portion of carbon mixed with BaCO_3 .

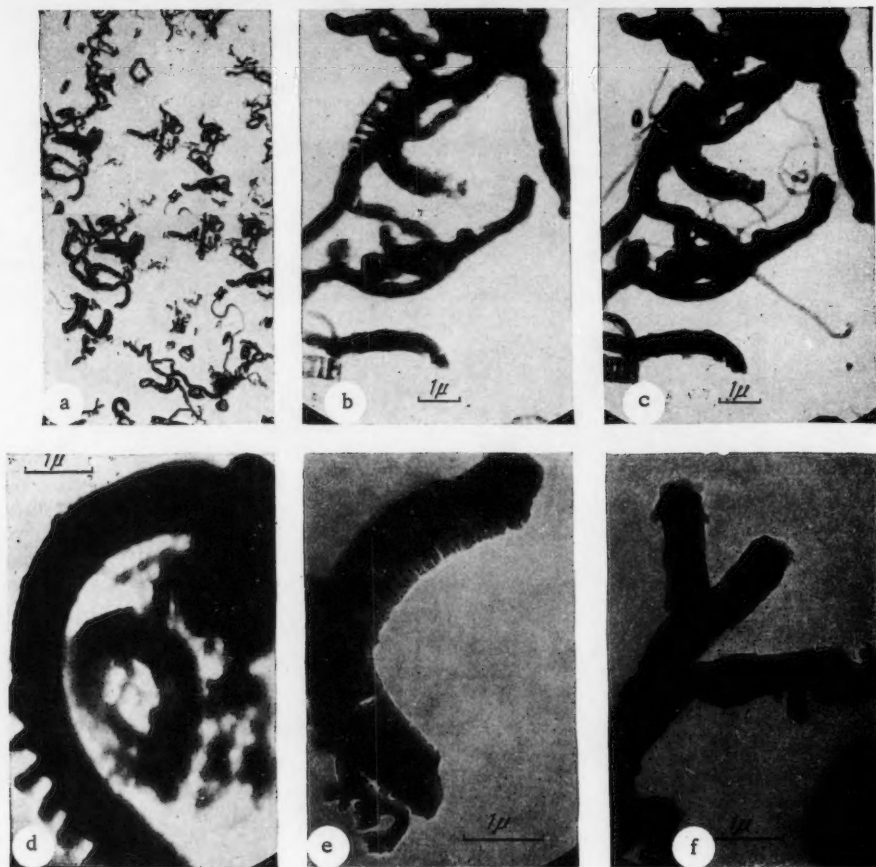


Fig. 2. Microphotographs of carbon dendrites under an electron microscope (the carbonaceous substance obtained upon decomposing *n*-hexyl alcohol on nickel at 600° during three hours): a) the general appearance of the carbonaceous substance stripped from the nickel sheet. This substance consists of a tangled fibrous mass of dendrites; magnification 2000x; b) underexposed; c) superexposed photograph of one and the same region at a magnification 8500x. On the underexposed photograph offshoots, at the side of the main dendrite stem, in the form of a comb are visible. On the superexposed one fine carbon hairs 500 Å appear. At the extremities of several dendrites the conical caps terminating them are visible; d) a dendrite with side offshoots under an angle of 90°; magnification 13,800x; e) a single curved dendrite with a clearly developed stratification; magnification 15 700x; f) a branched dendrite with two side offshoots under an angle of 60°; magnification 15 700x.

high electric conductivity, which considerably exceeded the conductivity of a carbon sample freed of nickel, we have established the metallic nature of the nickel in the deposits. In its magnitude the ferromagnetism of the carbonaceous substance, as was determined qualitatively on a Faraday torsion balance, approaches that of pure nickel. The absence of nickel carbides in the carbonaceous substance also follows from the fact that our experiments were carried out at temperatures much higher than their upper stability limit (400°, according to [16,17]).

TABLE 3. The Way in which the Evolution Rate and the Composition of the Gaseous Products in the Decomposition of *n*-hexyl Alcohol on the Nickel Sheets Change in the Course of Time.

Temperature °C.	Time, hours	Rate of gas evolution, ml/min	Gas composition, vol. %			
			H ₂	C _n H _{2n} (C ₂ H ₄)	C _n H _{2n+2} (CH ₄)	CO
445	1	10	13	9	76	1
	2	13	13	9	77	1
	3	—	—	—	—	—
	4	15	42	5	46	9
	5	17	56	4	24	16
	6	18	58	5	22	17
535	1	3	48	31	24	6
	2	5	34	22	9	4
	3	6	55	21	12	5
600	1	40	17	37	28	18
	2	15	12	42	29	17
	3	15	12	42	28	14
	4	12	—	—	—	—
800	1	120	35	5	29	30
	2	123	—	—	—	—

The general pattern of the change in composition of the decomposition for ethyl alcohol and that for cyclohexanol are similar and, therefore, in order to save space we do not give the data for these cases.

TABLE 4. Elementary Analyses of the Carbonaceous Substance Obtained upon Decomposing Alcohols on Nickel Sheets.

Alcohol fed	Temperature °C	Composition, vol. % (mean of 2)		
		C	H	C (from diff.)
<i>n</i> -Hexyl alcohol	445	94.02	0.12	5.86
<i>n</i> -Hexyl alcohol	600	96.91	0.66	2.43
Cyclohexanol	600	95.31	0.76	3.93
Cyclohexanol	820	98.91	0.10	0.89

is along screw dislocations starting around a certain disturbance, which originates the primary needle of the dendrite. As is well known [19-21], even for isometrically developing crystals of various substances it is characteristic that the growth of new layers takes place along screw dislocations. Screw dislocations in synthetic charcoals are even no rare phenomena and they have been noticed in many papers [22,23].

The data on carbon formation on nickel sheets which we have obtained are in complete agreement with the indicated assumptions on the conditions and mechanism of dendrite nucleation and with growth along screw dislocations. On the microphotographs of the carbonaceous substance under the electron microscope (Fig. 2) the characteristic shapes of stratified dendrites (a,e), dendrites with secondary offshoots under an angle of 90° (c,d), dendrites branched under an angle of 60° (f) and even fibers without offshoots at their sides (a,c) are clearly visible. Growth lamellas on the "primary needles" and constrictions where side offshoots start are conspicuous (b,e,f). It is true that, in the case of these carbon dendrites, the "needles" are no straight elongated formations but appear as various kinds of curved fibers with varying thickness. Bending of the dendrites during their helical growth may be caused by

RESULTS

All facts noted, namely, that the carbonaceous substance is deposited irregularly over the surface of the nickel sheets, nickel is corroded and transferred to the carbon deposits, the catalytic activity has a maximum after carbon has been deposited during 2-3 hours on a working catalyst, are in agreement with the supposition that the covering by carbon takes place in the form of dendrites. The direct observation of the dendritic structure in the carbonaceous substance confirms the rightness of this approach to an explanation of the phenomena found.

It is known that formation of dendrites, instead of crystals of usual shapes, takes place under conditions of rapid growth in those cases where the one-component medium is contaminated by impurities or where the medium from which the crystallization occurs consists of many components [18,19]. As a result of adsorption or chemisorption of impurities the crystallizing substance is deposited unilaterally on the crystal nucleus so that an elongated crystal, a needle, grows. The "needle" while growing penetrates the crystallization medium, as it were, repelling the impurities. By the lowered impurity concentration in some places around the "primary needle" or for some other reasons the growth of a "secondary needle" dendrite, which linked by a small stem to the "primary" one, may start. In just the same way a "tertiary needle" may germinate and so on. A branching dendrite is formed. The concentration distribution of the original material around the growing "needles" may also influence the growth of the branched dendrites. For instance, in the case where two nucleating protuberances lying on one line are formed, the condition that growth occurs in the direction of easiest supply of original material makes that the two growing "needles" of the branching dendrite part under an angle of 60° and this gives a certain displacement of the successive layers added. Since the crystal grows in the form of a branched dendrite, it can by-pass the unfavorable regions in the medium and the foreign particles hindering its growth. One of the main ways in which new layers are formed on the growing dendrites

very small variations in the conditions of coal formation resulting in a higher rate of coal deposition at one side of the dendrite and in systematic local disturbances in the thickness of each successive turn of the helix. In their structure, shape and sizes the discussed dendrites differ from the hollow carbon fibers which have been found previously [9,10], when carbon monoxide was decomposed on iron, cobalt and nickel catalysts. Obviously, only the fine (ϕ 0,05 μ) nonbranched fibers (2,c) are analogous to the latter. However, from the photographs which we have taken it is impossible to tell whether they are hollow formations or compact bodies. At the end of the dendrites and fibers one may note conical growth protuberances, which crown them (2 b,c,e) and are characteristic for dendrites growing by means of screw dislocations [19].

According to x-ray measurements, the metal structure has been put in a better order and its single crystals have turned greater by the participation of the nickel sheets in the catalytic experiments. Recrystallization of nickel also manifests itself in the fact that the metal appears in the carbonaceous substance and the tars. All this indicates that an active migration of nickel atoms takes place over the catalyst surface along the coal and that there are present some metalorganic compounds of the type: diphenyl-, phenanthrene, coronene-nickel [24] by means of which, possibly, the migration too of nickel along the surface and its transfer via the vapor phase are effected. As we have proved [15], under conditions analogous to those of the present experiments, the decomposition products of the alcohols studied always contain diphenyl, phenanthrene, coronene and other condensed aromatic hydrocarbon and, therefore, the formation of the compounds mentioned above is quite possible. It is also possible that nickel carbonyl is the volatile metalorganic nickel compound which brings about the transfer of this metal. However, here a doubt arises whether nickel carbonyl might exist for a short time under the conditions of the experiments, for it is unstable above 200°. Polycondensation of any metalorganic nickel compound with the material of a growing carbon dendrite results in an increased amount of carbonaceous material and in the formation of nickel crystals.

In the carbonaceous substance the nickel is present in the form of more or less large crystals and it is not dispersed as separated atoms through the carbon; its crystals become greater, when the carbonaceous substance is obtained at a higher temperature and the crystal size depends on the formation rate of carbon. For instance, in the decomposition of *n*-hexyl alcohol at 600° the formation rate of carbon is higher than that in the case of cyclohexanol and, judging from the photometric records of the corresponding x-ray patterns, the nickel crystals in the coal obtained are smaller in the former case. On the other hand, the carbonaceous substance obtained at 820° has an x-ray pattern in which nickel gives isolated dashes and points, which indicates that the crystals are large. According to just these x-ray data, the carbonaceous substance obtained at 600° has a more regular structure than has the substance obtained at 450 or 800°. A calculation from the x-ray patterns gives the following values for the distances between the lattice planes in the carbonaceous component and nickel:

carbon $a=2,4-2,5$;	$c=6,7-6,8$
nickel $a=2,6-2,7$;	$c=4,3-4,4$

The obtained data agree with known values from the literature for the interplanar distances in graphite [25] and hexagonal nickel [26].

The fact that the value of the parameter a for the carbonaceous substance is nearly equal to that for nickel, obviously, is of decisive importance in the joint formation of nickel and graphite crystallites. It is evident that the hexagonal graphite lattice determines the lattice structure of the nickel crystallite growing on its surface. Owing to this the nickel crystallite formed jointly with the carbonaceous substance grow in a hexagonal and not in the usual cubic one and this enables them to replace, as it were "isomorphously", parts of the carbonaceous substance. It is quite probable that the nickel crystallites are also dendrites and, since they are formed simultaneously with the carbon dendrites, they intergrow with the latter in some way. For instance along screw dislocations of a carbon dendrite helical nickel layers may wedge in or a nickel dendrite may be the pivot of a carbon dendrite. Other assumptions may also be proposed to explain the joint formation of carbon and nickel dendrites. It is even possible that the carbonaceous substance contains, besides dendrites, isometrically developed nickel crystals which are analogous to the previously observed [10] octahedral nickel and cobalt crystallites at the ends and in the central part of the hollow carbon fibers. However, in our present case isometric crystals, even if they are present, cannot be octahedra, since the nickel in the carbonaceous substance crystallizes in a hexagonal lattice.

The noted fact that the lattice type of the crystallizing substance is determined by the lattice parameters of the solid base on which it is deposited indicates that there is a strong crystallochemical interaction between the carbonaceous substance and hexagonal nickel and it is a good example proving the importance of geometric conformity, which, according to the multiplet theory, is one of the conditions for catalysis. A similar phenomenon

has been noted by Dankov [27] in a case where monomolecular layers of a new phase were formed on the surface of a crystalline solid.

From the microscopic investigation of the nickel sheets after the carbonaceous substance had been removed mechanically it follows that the surface of the sheet is strongly corroded. The corrosion is brought about by cavities which lie at the bases of large dendritical islets of the carbonaceous substance and are filled with a loose mass of carbon. It is evident that the formation of cavities in the nickel sheets is related to the deposition of carbon dendrites and the appearance of nickel in the carbonaceous substance, that is, the cavities are the places where the volatile metalorganic nickel compounds carrying nickel into the vapor phase are formed. Although these compounds here are partly decomposed within the cavities under formation of carbon and nickel, most of them are transported out of the cavities. Thus, the active centers for carbon deposition on nickel and the places where it is most intensively attacked under formation of volatile organic nickel compounds are one and the same formations.

The fact that the catalytic activity of these sites is preserved after the surface layers of nickel together with their active centers have been stripped off many times while the cavities are deepened compels one to suppose that the active centers are constantly regenerated on the bottom of the cavity and that their specificity is preserved. This property of the said sites can be easily explained, if the active sites of carbon formation are related to screw dislocations terminating on the surface of the nickel single-crystals. When one strips off successively layers from a screw dislocation (untwining the helix), the dislocation itself will be preserved and, consequently, also its properties. The irregular way in which in our experiments the nickel sheets are covered with carbon, evidently, is related to the irregular distribution of the endpoints of screw dislocations on the sheet surfaces. The complete absence of carbon formation on sheets polished without development of dislocations is an indirect indication that the active sites of carbon deposition are related to defects in the nickel lattice. So, a carbon dendrite growing on a screw dislocation of nickel as active center is able to attack rapidly its base and to grow not only above the surface of the nickel sheet but even to penetrate into it. A somewhat similar phenomenon was observed by Frank [28] in the formation of tin dioxide dendrites on tin.

The joint growth of carbon and nickel dendrites makes clear which is the reason for the observed increase in the catalytic activity of the nickel sheets in the initial stage of their covering by carbon. The carbon dendrites, which contain dendrites of the catalyst substance, do not merely raise the surface area of the catalyst but increase the number of active centers and the dislocations formed on the catalyst dendrites may be such centers. The increase in formation rate of carbon in the initial period, obviously, is connected with the growth of secondary and tertiary "needles" of the nickel dendrite. The decreased catalytic activity at a great extent of carbon deposition, obviously, is connected with the greater covering by carbon and the elimination of dislocation in the catalyst. A similar explanation may be extended to other cases too as have been recorded in the literature [1-4, 29-31], where in the initial stage of carbon deposition the activity of the catalyst is raised.

The great role which formation of catalyst dendrites plays in raising the catalytic activity allows one to suppose that the essential point of catalyst activations, as are alternative oxidation and reduction, prolonged oxidation and other special treatments of catalysts, comprises the formation of catalyst dendrites, which raise the number of active centers and even change their specificity.

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SUMMARY

1. The carbon deposits formed in the decomposition of ethyl-, *n*-hexyl alcohol and cyclohexanol on nickel sheets at 450-820° have a dendritic structure. Stratified, nonbranched fiber-like dendrites and branched dendrites with conical terminations have been detected.

2. The carbonaceous substance of the dendrites has lattice parameters characteristic for graphite and contains from 1 to 6% metallic nickel crystallized in a hexagonal lattice. The formation of hexagonal, instead of cubic, nickel results from the two-dimensional geometric correspondence between the parameters of hexagonal nickel and graphite and from their crystallochemical interaction.

3. The terminations of screw dislocations, allowing carbon dendrites to grow on them just in the form of such dislocations, are the active centers for the deposition of carbon on nickel. At the same time these active centers are the suppliers of nickel migrating into the carbonaceous substance.

4. The enhanced catalytic activity, which for the catalyst getting covered with carbon is found during the first 2-3 hours of its use, is connected with the increased number of active centers, as results from the joint formation of nickel- and carbon dendrites.

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THE COMPENSATION EFFECT IN ACTIVATION PROCESSES FROM THE POINT OF VIEW OF STATISTICAL KINETICS

COMMUNICATION I. CALCULATION OF THE PRE-EXPONENTIAL FACTOR IN THE FORMULA FOR THE RATE OF THE PROCESS.

S. Z. Roginskii and Yu. L. Khait

Institute of Physical Chemistry, Academy of Sciences of USSR.

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In the kinetics of various chemical and physicochemical processes with Arrhenius temperature dependency of the constants:

$$K = K_0 \exp\left(-\frac{E_a}{RT}\right), \quad (1)$$

where E_a is much greater than RT , there is often observed an incommensurably small effect of change in the activation energy E_a on the rates of the processes [1-5]. In equation (1), T is the temperature of the system, and R the gas constant [1-5]. In order that such processes may still under these conditions be described by a simple equation of type (1), it is necessary to postulate that the pre-exponential factor K_0 in this equation is dependent on the value of E_a : that is that $K_0 = f(E_a)$. Thus, to secure concordance between equation (1) and experiment in a number of cases, it is necessary to suppose that this dependence on E_a is quite profound, and $f(E_a)$ may be expressed by an equation of the type:

$$f(E_a) = K_0^0 \exp(\beta E_a^n) \quad (2)$$

In view of the lack of experimental data on change of the energy E_a over a wide range (greater than a factor of 10), the value of n in equation (2) cannot be estimated very precisely [3,4], although the value is usually taken as unity. Consequently, it is possible to postulate the formula below for a satisfactory description of the experimental data:

$$K = K_0^0 \exp\{\beta E_a^n\} \exp\left\{\frac{E_a}{RT}\right\}, \quad (3)$$

which is obtained by substituting relationship (2) in equation (1). The two exponential functions in equation (3) vary in opposite directions with change in E_a , and so compensate each other. This effect has been given the name of "compensation effect". Thus, analysis of the experimental data makes it possible to affirm that, for a wide range of processes, systems and conditions, considerable deviations are found from the Arrhenius equation, which is therefore an insufficient approximation for such processes.

The origin of the compensation effect has not up to the present been satisfactorily elucidated [1,2,5]. Its appearance in processes and systems of very different character suggests that we should look for some link between it and the general laws of physical kinetics, and not merely a connection with specific peculiarities of particular systems and processes.* As a study of the experimental material shows the compensation effect is characteristic for condensed systems [2]. Certain new possibilities for the theoretical study of the compensation effect were opened up recently [2] by successive statistical approaches to the activation process, without the use of detailed mechanical

* Of course specific peculiarities of particular systems will be found, but these will either intensify or weaken that part of the compensation effect which is general for a wide class of processes and systems.

models of the systems and special mechanisms for the processes. In the present work, the conception put forward in [2] is elaborated and developed further, while, as before, the problem is limited to the investigation of general statistico-kinetic causes which permit of the deduction of deviations from the simple Arrhenius formula, and which lead to a relationship of the type (3).

Calculation of the pre-exponential factor. The most widely used schemes for calculating the rates of activated processes in solid and liquid systems are the method of Frenkel' [6], and the theory of absolute reaction rates [7]. But neither of these theories takes into account the presence of a strong bond between the particles of a condensed body, upon which the collective nature of their movements is based. Both theories are limited by their individualistic consideration of the movement of individual particles of the substance in the accomplishment of the elementary act of transition across the barrier, and fail to take account of the effect of this event on the surrounding particles. Frenkel' referred to the contradictory nature of such a procedure in constructing the elementary theory of activation processes in condensed bodies [6], but he observed [6] that, in considering activation processes in solid and liquid systems, the atoms should be considered as a single bonded system, in which collective oscillations take place. This is similar to the Debye theory of heat capacity. The transition of each particle through the barrier is accompanied by a change in the condition of the neighbouring particles, which have a strong interaction with one another, and in their turn interact with further particles, etc. Thus, some dislocation in the system must be considered, associated with local regrouping of the particles. Hence also, the "individualistic" consideration of the separate transitional acts through the barrier, which is applicable to gases in which binary collisions can be contemplated, meets with serious difficulties when we come to consider activation processes in condensed bodies. The "individualistic" approach to activation processes in such bodies is founded on theories of instantaneous shedding of excess energy by the individual atoms, and its instantaneous concentration on the particles [6]. Such theories are practically equivalent to the assumption of an infinitely high rate of transfer of energy in the system.

In addition, in considering the probability of the transition of individual particles through the barrier without taking into account the change in the condition of the surrounding medium, it is necessary to employ the thermodynamic theory of fluctuations, and in particular the Boltzman principle, to the individual particles. But it is well known that this thermodynamic theory of fluctuations is only applicable to basic systems containing a sufficiently great number of particles [8,9]. Failure to take into account the collective nature of the movements of atoms and molecules in the theory of reaction rates and the elementary theory of Frenkel', has also led to the separation of the theory of activation processes in solids from the contemporary quantum theory of solids. All this shows that the "individualistic" approach to elementary processes in condensed bodies is unsatisfactory.* In the subsequent consideration of activation processes in solid (and liquid) bodies, it will be necessary to take the collective character of the particles' movement into account. This will be in harmony with the current quantum theory of solids (see, for example, [10]). In analysing the rate of activation processes, we shall commence with the relationship obtained by one of us [11] by means of a statistical method of calculating the rates of activation processes. This permits, in considering the elementary act, taking into account the collective nature of the movement of particles in a condensed body, and of the finite magnitude of the rate of energy transfer within it. It will be shown below that, starting with the basic relationship obtained by the method described in [11], one may derive without additional assumptions the dependence between the pre-exponential factor and the activation energy; and that this within certain limits corresponds to formula (3). In the course of this, the interaction between the particles of a substance is found in the long run to be included in the phenomenological characteristics of the system (heat capacity, activation energy, etc.). We shall formulate the basic physical assumptions developed in [11] in a form suitable for describing the compensation effect.

For the definition of the activation process, we shall name the process consisting of the ultimate total of the elementary acts of movement or rearrangement of the particles of the substance, proceeding up to the final time interval. Each of the elementary acts is based upon the fact that an energy E' , exceeding some critical value $E \gg kT$, is collected by chance in separate degrees of freedom (individual bonds), within a small volume d^3 (where d is of the order of the linear magnitude of the region occupied by a single atom). The energy $E' \geq E$, necessary for the accomplishment of a single act, is accumulated in the volume d^3 at the expense of some reduction in the energy of the surrounding particles in the system. Since the mean velocity v of the transfer of energy within the

* Frenkel' [6] clearly formulated physical premises for the "individualistic" method in condensed bodies, although the authors of the reaction rate theory [7] did not do this. This, however, does not materially alter the case.

system is finite, and the duration τ of the elementary act is small, only those particles will "participate" appreciably in the individual act which are located within a macroscopically small volume l^3 , surrounding the place in which the elementary act occurs. The magnitudes l^3 may be estimated, if account is taken of the fact that the rate of inflow of energy into each volume l^3 through its surface is limited. We may therefore derive the dimension l in such a way that the small time $\tau \approx \frac{1}{\nu}$, permits the energy of the volume l^3 to change on account of the change in energy in the other particles in the system by the mean value $\Delta U(\tau)$, lying lower than the value of E [11,12]. In such a case, during the time interval τ the volume l^3 appears to a first approximation to be closed, in relation to the single act of transfer through a barrier of height E . At the same time it is required that the mean energy of thermal motion, U_T of the volume l^3 shall be greater than E . This permits of limiting the dimensions of l^3 by means of the conditions in [11], thus:

$$L^2 \leq \frac{Ed^3}{ah\nu}, \quad L^3 \gg \frac{E}{akT}d^3, \quad (4)$$

where a is the number of degrees of freedom of a definite type (such as "lattice" degrees of freedom in a solid within the volume d^3); h =Planck constant divided by 2π . If, within the time interval τ , a single act of the process considered is accomplished within the volume l^3 , then the contribution of those parts of the body lying outside the region l^3 surrounding the place where the act takes place, may be neglected. At the same time it is necessary to take into account the considerable time "freezing" of the overwhelming majority of degrees of freedom of the volume l^3 , arising from the fact that the energy $E' \geq E$ is assembled by change in certain degrees of freedom at the expense of the remainder. In connection with this we consider two types of functions [11,12]:

1. Chance deviation of the energy U of the region l^3 from the mean value U , owing to transfer of energy between a certain nucleus l^3 and the other particles in the system.
2. A chance act of concentration of the energy $E' \geq E \gg kT$ in individual degrees of freedom within the volume l^3 for a fixed value of U . There exists a conditional probability, not equal to zero, that, during the course of the time interval τ (during which the region l^3 is practically closed), unit act of the process under consideration takes place. If the elementary act is not accomplished during the time τ , the following time interval τ must then be considered, with another energy U of the region l^3 , and another conditional probability of the single process, etc. Thus, the conditional probability of the single act within one region l^3 should be averaged throughout all time intervals τ . But, because of the ergodic* property of the time average, we may substitute the average according to the probability of the corresponding states. These considerations make it possible to avoid the description of a system of strongly interacting particles by the methods of mechanics by means of the functions (operators) of Halmilton and Lagrange, and to pass over completely to a statistical (theoretico-probability) point of view. This method has the advantage that it permits of the avoidance of difficulties associated with mechanistic problems of many particles which interact strongly with each other. In the final formulas the interaction taking place between particles of a substance, is found to be included in the phenomenological constants of the substance (activation energy, heat capacity, conductivities, etc.). We shall therefore in what follows not discuss the mechanistic behaviour of individual particles of the substance, but shall interest ourselves in the mean probability W , related to unit time, of the completion of the elementary act of the activation process of a definite type, within one microvolume l^3 . If the volume l^3 is sufficiently small, and $E \gg kT$, it is possible to suppose that within this volume at time τ there is performed (on the average) not more than one elementary act of the activation process. This permits the activation process to be considered as a discontinuous chance process [11-13]. Related to unit time, the number of elementary acts of the activation process of a definite type within a volume V may be calculated from the equation in [11]:

$$N_1 = \frac{V}{l^3} W. \quad (5)$$

Taking account of the fact that the occurrence of the elementary act of the activation process produces an intermittent change in the state of the volume l^3 , in which this act took place (the act of the discontinuous chance process of [13]), it may be affirmed [11,12] that the probability W is obtained by integration of the expression:

* Transliteration of Russian—Publisher..

$$\varphi(U) = \frac{kT(U-E)}{\hbar} \exp\left[-\frac{F-F_0}{kT}\right] \exp\left[\frac{S(U-E)-S(U)}{k}\right] \quad (6)$$

through all permissible values of the energy U in the region l^3 . Here F , $S(U)$, $S(U-E)$, $T(U-E)$ are respectively the local free energies, entropies and temperatures in the volume l^3 , corresponding to the energies U and $(U-E)$, while F_0 is the mean value of the free energy in the region l^3 . The entropies, free energies, etc., must be related, not to all the degrees of freedom of the volume l^3 , but only to a definite type of degree of freedom, such as the "lattice" degree of freedom, to the electronic degree of freedom, etc. The question as to which degrees of freedom are to be taken account of is to be resolved from the actual nature of specific systems and processes.

The equation (6) possesses a sharp maximum. This permitted, without carrying out the integration, of obtaining the approximate formula of [11]:

$$W = qW_0 \exp\left\{-\frac{E}{kT}\right\} = \frac{kTq}{\hbar} \exp\left\{-\frac{E}{kT}\right\}, \quad (7)$$

where the dependence of W_0 on E is not considered, q is related to the concentration of particles (whose bonds suffer rupture) involved in the process under consideration. We now suppose that from the relationship:

$$W = q \frac{k}{\hbar \sqrt{2\pi}} \int T(U-E) \exp\left\{\frac{(\Delta U)^2}{2\alpha^2}\right\} \exp\left\{\frac{S(U_0-E)-S(U)}{k}\right\} \frac{dU}{\alpha} \quad (8)$$

without additional assumptions, we may now (within definite limits) arrive at the relationship between W_0 and E . Formula (8) is obtained by integrating (6) with respect to U with substitution of the Boltzmann factor,

$$\left\{-\frac{F-F_0}{kT}\right\} \quad (A)$$

by the Gaussian distribution*,

$$\frac{1}{\sqrt{2\pi\alpha^2}} \exp\left\{-\frac{(\Delta U)^2}{2\alpha^2}\right\}, \quad (B)$$

where $\Delta U = U - U_0$, and

$$\alpha^2 = kT^2C \quad (9)$$

which is the mean square of the fluctuation of the energy in the volume l^3 . C is its heat capacity. In this treatment we neglect any correlation between the regions l^3 . In many cases, when the measurements are carried out under ordinary conditions, and without specially wide temperature variations, the heat capacity may be treated as independent of temperature, and we may suppose that:

$$\frac{\partial^n C}{\partial T^n} \approx 0 \quad (n = 1, 2, \dots) \quad (10)$$

If we express the function $S(U-E)$ as a series in increasing values of E , and taking account of (10), we obtain:

$$\frac{S(U-E)}{k} = \frac{S(U)}{k} - \frac{C}{k} \sum_{n=1}^{\infty} \frac{E^n}{n \cdot [CT(U)]^n}, \quad (11)$$

where $T(U)$ is the local (temporary) temperature of the region l^3 , corresponding to the energy value U . Since $E < CT$,

* The Boltzmann principle is valid only in cases for which the Gaussian distribution of the corresponding magnitudes applies [7].

the series converges in successive members. We introduce the notation $X = \frac{E}{CT(U)}$ and calculate that

$$-\sum_{n=1}^{\infty} \frac{X^n}{n} = \ln(1-X). \quad (C)$$

Then equation (11) takes the form

$$\frac{S(U-E)-S(U)}{k} = \frac{C}{k} \ln \left[1 - \frac{E}{CT(U)} \right]. \quad (D)$$

Hence (11) is equivalent to the relationship:

$$\frac{S(U-E)-S(U)}{k} = \ln \left[1 - \frac{E}{CT(U)} \right]^{C/k} \quad (11a)$$

The quantity $\frac{C}{k}$ is of the order of the number of particles in the region l^3 ; i. e. $\frac{C}{k} \approx \frac{l^3}{d^3} \gg 1$, and hence $\frac{C}{k}$ represents a large number. On the other hand it is known that:

$$\lim_{p \rightarrow \infty} \left(1 - \frac{y}{p} \right)^p = e^{-y}. \quad (E)$$

Writing $y = \frac{E}{kT(U)}$, and taking account of the fact that the ratio C/k is large, we may rewrite (11a) in the form:

$$\frac{S(U-E)-S(U)}{k} = -\frac{E}{kT(U)}. \quad (12)$$

Inserting (12) in (8), we find:

$$W = \frac{k}{\sqrt{2\pi} \hbar} \int T(U-E) \exp \left\{ -\frac{E}{kT(U)} \right\} \exp \left\{ -\frac{(\Delta U)^2}{2\alpha^2} \right\} \frac{dU}{\alpha}. \quad (13)$$

The integral in (13) has not, in its general form, been calculated. Therefore, we take advantage of equation (10) and present $T(U)$ and $T(U-E)$ in the forms:

$$T(U) = T + \frac{\Delta U}{C}; \quad T(U-E) = T + \frac{\Delta U - E}{C}. \quad (14)$$

Inserting (14) in (13) we obtain:

$$W = \frac{kT}{\hbar \sqrt{2\pi}} \int \left(1 + \frac{\Delta U - E}{CT} \right) \exp \left\{ -\frac{(\Delta U)^2}{2\alpha^2} - \frac{E}{kT \left(1 + \frac{\Delta U}{CT} \right)} \right\} \frac{dU}{\alpha}.$$

For the evaluation of the integral in (15) we make use of the fact that it is usually true that $(\Delta U/CT)^2 \ll 1$. Then, taking account of

$$\frac{1}{1 + \frac{\Delta U}{CT}} \approx 1 - \frac{\Delta U}{CT} \quad (F)$$

and making the substitution $y = \frac{\Delta U - E}{\alpha}$, we rewrite (15) in the form:

$$W = \frac{kT}{\hbar} \exp\left\{\frac{E^2}{2\alpha^2}\right\} \exp\left\{-\frac{E}{kT}\right\} \frac{1}{\sqrt{2\pi}} \int_{-\infty}^{\infty} \left(1 + y \frac{\alpha}{CT}\right) \exp\left\{-\frac{y^2}{2}\right\} dy, \quad (16)$$

where account is taken of: $U = d(\Delta U - E)$, and infinite limits of the integration are used. The latter, in view of the rapid decrease of the function within the integral sign has practically no effect on the result. The integration in (16) is an elementary matter and gives (17) below:

$$W = \frac{kT}{\hbar} \left(1 + \frac{kT}{\alpha}\right) \exp\left\{\frac{E^2}{2\alpha^2}\right\} \exp\left\{-\frac{E}{kT}\right\}. \quad (17)$$

Hence we find the preexponential function in the form:

$$W_0 = \frac{kT}{\hbar} \left(1 + \frac{kT}{\alpha}\right) \exp\left\{\frac{E^2}{2\alpha^2}\right\}. \quad (18)$$

To explain the physical principles of the phenomenon of the compensation effect, it is convenient to carry out the calculation in another way. The expression (6) (the same as in the function inside the integral sign in (8) and (13) has a sharp maximum at a certain value of the energy [11]:

$$U_m \approx \bar{U} + E. \quad (19)$$

Hence the probability W may be calculated, not by carrying out the integration with respect to U in (8), but by considering the values corresponding to the maximum in the sub-integral expression.* Hence, by means of (6) we may write:

$$W \approx q \frac{kT(U_m - E)}{\hbar} \exp\left\{-\frac{F_m - F_e}{kT}\right\} \exp\left\{-\frac{S(U_m - E) + S(U_m)}{K}\right\} \quad (20)$$

Using the subintegral function in (13), obtained from (6), we rewrite (20) in the form:

$$W \approx q \frac{kT(U_m - E)}{\hbar} \exp\left\{-\frac{(\Delta U_m)^2}{2\alpha^2}\right\} \exp\left\{-\frac{E}{kT(U_m)}\right\}, \quad (21)$$

where $T(U_m)$ is the temperature corresponding to the energy U_m , and $\Delta U_m = U_m - \bar{U} \approx E$. By means of (14) and (19) we obtain:

$$T_m = T(U_m) \approx T + \frac{E}{C}. \quad (22)$$

The presence of the sharp maximum in the expression for the probability of the elementary act (Fig. 1), denotes that of the number of elementary acts carried out, the great majority occur within those regions U^3 , the energy U_m of which exceeds the mean energy \bar{U} by the value E , while the local temperature is $T(U_m)$, and exceeds the mean temperature T by the value:

$$\Delta T_m \approx \frac{E}{C}. \quad (23)$$

Making use of (10), and also assuming that

$$\left(\frac{E}{CT}\right)^2 \ll 1,$$

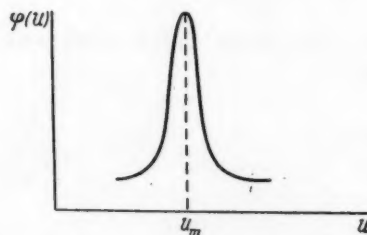


Fig. 1

* A similar method has also been used in [11], but the calculation went only as far as the first approximation, and hence the relationship between W_0 and E considered here was not obtained.

we may write:

$$\frac{E}{kT(U_m)} = \frac{E}{kT\left(1 + \frac{E}{CT}\right)} \approx \frac{E}{kT} \left(1 - \frac{E}{CT}\right). \quad (24)$$

Substituting (24) in (21), and noting that, according to (19):

$$\Delta U_m = U_m - \bar{U} = E, \text{ a } T(U_m - E) = T(\bar{U}) = T \quad (G)$$

while $kCT^2 = \alpha^2$, we obtain the formula:

$$W = q \frac{kT}{h} \exp\left\{\frac{E^2}{2\alpha^2}\right\} \exp\left\{-\frac{E}{kT}\right\}, \quad (25)$$

which, within an accuracy of one order of magnitude, is in harmony with (17). This formula, after simple rearrangement in some sense the reverse of (24), may be obtained in a form superficially similar to that of Arrhenius. For this purpose we use the simple relationships (within the same approximations):

$$\frac{E^2}{2\alpha^2} - \frac{E}{kT} = -\frac{E}{kT} \left(1 - \frac{E}{2CT}\right) \approx -\frac{E}{kT \left(1 + \frac{E}{2CT}\right)}. \quad (H)$$

Then formula (25), and (17) also with an accuracy corresponding to an insignificant multiple, may be written in the following form:

$$W = q \frac{kT}{h} \exp\left\{-\frac{E}{kT_{\text{eff}}}\right\}, \quad (26)$$

where,

$$T_{\text{eff}} = T \left(1 + \frac{E}{2CT}\right) \quad (27)$$

which denotes the effective temperature, which exceeds the mean temperature by the magnitude:

$$\Delta T_{\text{eff}} = \frac{E}{2CT}. \quad (28)$$

By means of (5) we now obtain the formula:

$$N_1 = q \frac{KTV}{hI^3} \exp\left\{-\frac{E}{kT_{\text{eff}}}\right\}, \quad (29)$$

which permits of the calculation of the number of elementary acts in unit time of the activation process of a definite type taking place within the volume V.

RESULTS

The formulas (17), (25), (26) and (29) obtained above show that, within certain limits there arises from formulas (6) and (8), without additional assumptions, the relationship between the pre-exponential factor and the activation energy. Consideration of these relationships will be deferred until a later communication. We shall here deal briefly with the limits of applicability of these formulas, using the postulates made in [11].

1. It has been assumed that in each individual act the whole of a region l^3 takes part, the volume being that in which appreciable change takes place while the direct effect of the remaining part of the system on the elementary act may be neglected. This postulate signifies that a difference exists between the immediate neighbourhood

of the place where the elementary act has occurred, and the remainder of the system, in their effect on the single act. The effect of the latter leads to a relatively smooth change in the physical magnitudes in space and time, which may be described directly as macroscopic. But the details of the rapid processes occurring within the region l^3 during time intervals appreciably smaller than, cannot be described by the terms of macroscopic physics. This only permits of a determination of the probability of the final result of many microscopic processes [14], as has been done both in the present work, and in previous ones [11,12].

2. We have neglected above the correlation between the various volumes l^3 . Taking into account that, according to equation (4), the regions l^3 still contain a large number of molecules, we may assert that the formulas obtained represent a step forward compared with the elementary theory, where no account is taken of the link between even strongly interacting particles. The regions l^3 satisfy the condition:

$$\frac{L_2}{d^2} \ll \frac{L_3}{d^3}, \quad (30)$$

and therefore undergo interaction relatively weakly, and under definite conditions their correlation may be neglected. Generally speaking, however, this correlation should be taken into consideration. This may be done within the framework of the correlation theory of stationary chance processes (cf, for example, [13]), by means of the stochastic model presented in [11,12].

3. It was supposed in [11] that during the time τ in the regions l^3 , not more than one elementary act of the activation process was accomplished, and that the probability of the completion of this one act does not depend on the prehistory. This assumption corresponds to the Poisson process [13]. Because of the fact that $\tau \approx \frac{l}{V}$ is a relatively small quantity, while $E \gg kT$, it may be asserted that:

$$\tau \ll 1/W, \quad (31)$$

which justifies the assumption made.

4. It has been assumed that the change in the energy U of the region l^3 is subject to a Gaussian distribution. This assumption corresponds to the thermodynamic theory of fluctuations [8,9], and is justified by the fact that the volume l^3 possesses a large number of degrees of freedom, and great deviation is of low probability. The Gaussian distribution of the energy U in the region l^3 is a conclusion drawn in [11, 12] from the stochastic model of the system, where N -fold stationary Gaussian processes are considered.

5. It has been assumed that the thermal capacity C is independent of the temperature. This assumption is justified when the temperatures are not very high or very low and for relatively small intervals of temperature change, or, if the heat capacities of the degrees of freedom considered depend only slightly on T .

6. It has been assumed that

$$\left(\frac{E}{CT}\right)^2 \ll 1 \quad (32)$$

Since the region l^3 contains a large number of degrees of freedom, and it has been chosen in such a way that the condition $U_T > E$ is fulfilled, the inequality in (32) is fulfilled.

7. It has been assumed that energy transfer in the system may take place without transfer of the substance, and that the particles of the substance, owing to their strong interaction, do not during times of the order of $1/W$ succeed in leaving the volume l^3 , so that the composition of the substance in the region l^3 is practically unchanged during the time of the order of $1/W$. This assumption refers specifically to a condensed body, where, in distinction from a gas, transfer of energy and transfer of mass are distinct from each other and proceed with entirely different velocities [14]: the latter process in condensed bodies occurs very slowly, while in the former the transfer of energy*

* "latter" and "former" have been transposed from the order in which they appear in the Russian text, since this plainly was the authors' intention - Publisher.

takes place rapidly (with the velocity of phonons of the order of $10^4 - 10^5$ cm/sec, or with that of electrons, of the order of $10^7 - 10^8$ cm/sec, etc). We may note also that the calculation carried out above has been performed with an accuracy of an order of magnitude. With these assumptions for reactions taking place in condensed phases, the compensation effect is revealed, though it is absent from the statistical theory of absolute rates. It should be emphasized that the fundamental factor expressed in equation (18) for the relationship between K_0 and T is not in harmony with the relationship obtained experimentally, either in the most common form $K_0 = K_0^0 \exp(\beta E_a^0)$, nor in the more general form (2). Actually, in all concrete experimental work β has been assumed to be independent of T . At the same time the expression $(2\alpha^2)^{-1}$, appearing in the pre-exponential factor $\exp(E^2/2\alpha^2)$, contains the quantity T^{-2} in a concealed form and, consequently, K_0 becomes a temperature dependent quantity, even more strongly so than the larger quantity E . The formulas obtained show that an Arrhenius dependence for the rates should be observed, but that by the use of this relationship the observed value of E should be less than the true value. At the same time, through α and N in equations (5), (17), (25) and (29) for the rates of processes, there enter in certain substantial characteristics of the substance. In this, in contradiction to the theory of the transitional complex, the definite physical constants of the condensed system are revealed as fundamental, and not the structure of the transitional state. These problems, and also the nature of the change entering into the theory of the compensation effect by taking into account the correlation of the processes taking place in different micro-zones, require special consideration.

By means of the relationships obtained in [11,12], it may be shown that calculation of the effect on the elementary act of the particles of a system lying outside l^3 , leads to a pre-exponential factor strongly dependent on E and practically independent of T .

SUMMARY

1. Analysis of the experimental data provides a basis for the supposition that general causes exist which give rise to the profound relationship between the pre-exponential factor and the activation energy. This relationship does not emerge from the theory of absolute reaction rates and the assumptions of Frenkel', which do not take into account the collective character of the movement of interacting particles in a condensed system.

2. Taking account of the collective character of the movement of the particles in a condensed system during the consideration of the elementary act, leads to an exponential relationship between the pre-exponential factor and the activation energy. Analysis of the premises lying at the basis of the relationships obtained, reveals certain possibilities for further communications.

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THE PHASE COMPOSITION AND TEXTURE OF ALUMINO-CHROME CATALYSTS PREPARED BY SIMULTANEOUS PRECIPITATION

A. M. Rubinshtein, A. L. Klyachko-Gurvich and V. M. Akimov

The N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of USSR.

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The study of the phase composition of alumino-chrome catalysts presents considerable difficulties, which have only recently been overcome by R. Davis and his colleagues [1], who have shown that these catalysts are a complex system of limited solid solutions of the components. A similar picture, though with other limits for the concentrations of the saturated solid solutions, has been arrived at by ourselves for the case of ferro-alumina gels [2]. This is fully understandable, since ferric oxide and chromium-III oxide are isomorphous, so that their behaviour when blended with alumina ought to be similar. Very interesting data on the magnetic character of alumino-chrome catalysts have been obtained by Eishens and Selwood [3,4]. However, the conclusions drawn in these works concerning the distribution of the components and the nature of the phase composition of the catalysts, need considerable rectification, since the authors did not take into account the probability of the formation of solid solutions among the components.

It is known that the conditions under which the catalysts are prepared may also exert influence on their phase composition and structure. We may give the following case as an example. Milligan and Merten [5] obtained amorphous structures with a wide range of concentrations of the components nickel oxide and alumina, while we ourselves [6], using the same ratio of concentration limits of these components, obtained high dispersed catalysts of nickel oxide and alumina with a clearly developed crystal structure, in spite of the fact that the conditions of thermal treatment were identical or very similar in the two cases. There is thus clearly indicated a difference in the conditions of precipitation. The conditions of precipitation exert an even greater effect on the texture of catalysts—on the magnitude of their specific surface, the specific volume and the pore radius. It seemed a matter of interest in this connection to conduct a repeat investigation of the phase composition and texture of alumino-chrome catalysts, to follow the effect upon them of the pH of precipitation, and the conditions of the thermal treatment, and also to study the change in structure after catalytic experiments: the results of this last are described in a separate article. The detailed structural characteristics of alumino-chrome catalysts are also found to be necessary for determination of their specific activity in dehydrogenation and dehydration reactions, in a similar way to that shown earlier [7] for the more complex alumino-chrome-potassium catalysts, which have been used successfully for the dehydrogenation of paraffins.

EXPERIMENTAL

In the alumino-chrome catalysts investigated, the concentrations of the components were varied from 0 to 100 mol.%, while catalysts containing 3, 15 and 100 mol.% chromium-III oxide were prepared at different precipitation pH values, the precipitation being carried out at room temperature by 10% ammonia solution from a mixture of solutions of aluminum and chromium nitrates in calculated quantities, diluted by the addition of water to a total volume of 1.5 liters. The final pH value at precipitation was determined potentiometrically (using potentiometer LP-5). The hydroxide precipitate was washed for removal of nitrate ions, filtered and moulded, and dried at 110° in air. It was then divided into separate portions and submitted to 6 hours ignition at 450° and 600°, two series of products being thus obtained, and numbered AKh-450 and AKh-600. The weight loss on heating to 1000° was used to characterize the residual water content in the products heated at 450° and 600° in an approximate way only, since the loss was partially accounted for by decomposition of chromium-VI compounds with the splitting off of oxygen.

X-ray phase analysis was carried out * by the powder method in RKD chambers having a cassette diameter of 57.3 mm; though some samples were examined in RKU chambers, which had greater resolving power (cassette diameter 114 mm), with the object of determining more accurately the lattice parameters of the phases participating in the catalyst composition. Exposure was carried out by means of filtered (nickel filter) K-series radiation of copper. Some catalysts were examined by means of K-series radiation of molybdenum, since it was found by Davis [1] that the η -phase of chromium-III oxide could only be observed with this radiation.

In identifying the crystalline phases of alumina, we have used the notation system described earlier [8]. In determining the parameters of the lattices, difficulties were encountered in the selection of the x-ray diagram lines formed at a sufficiently large angle of reflection and not overlapped by other lines, while at the same time sufficiently intense. The method used was to employ for rhombohedral crystals lines (123) and (103), and for cubic crystals lines (004) and (044). Taking into account the degree of accuracy with which the lines could be measured on the x-ray diagrams, and with which the effective radius of the cassettes could be found, the accuracy with which the parameters of the crystal lattices could be found was ± 0.03 Å for cubic phases, and ± 0.015 Å for rhombohedral phases. The characteristics of the chemical and phase composition of the catalysts studied are set out in Table 1. It should be borne in mind that for mixed catalysts the notations " γ - Al_2O_3 ", " Cr_2O_3 " and others in the Table, do not indicate that the pure components are in issue, but that solid solutions of the components occur with the corresponding spinel (cubic) and rhombohedral structures. More will be said on this in the discussion of results.

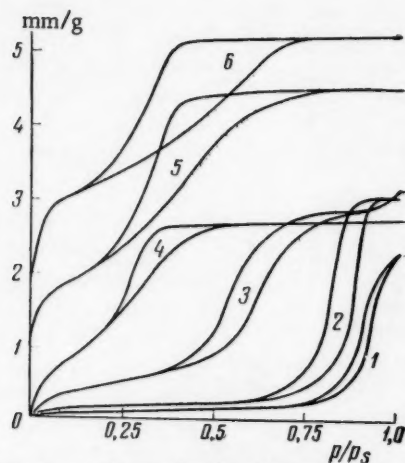


Fig. 1. Isotherms for the adsorption of benzene vapor on alumino-chrome catalysts ignited at 450° : 1) Cr_2O_3 -II; 2) 90% Cr_2O_3 ; 3) 75% Cr_2O_3 ; 4) 50% Cr_2O_3 ; 5) 25% Cr_2O_3 ; 6) 10% Cr_2O_3 . (The scales for curves 5 and 6 are shifted one and two units upwards respectively).

isotherms obtained, showing the change in their adsorption on the catalysts with sudden jumps in the composition of the catalyst, and curves for the distribution of pore volume according to radius, are shown in Fig. 1 and Fig. 2 respectively; while the characteristics of the texture of the catalysts are given in Table 2, in which r_m indicates the position of the maximum on the distribution curve.

The determination of the texture of the catalysts was also performed after their use in experiments on catalytic decomposition of absolute isopropyl alcohol at 245 – 350° , which will be described in subsequent communications from our laboratory. The measurements have shown that, after a few experiments (up to 5) under these conditions, the mean radius of the pores is not substantially changed in comparison to the initial value, while the value of S , if it changes at all, does so by only 5–10%, or about within the limits of experimental error.

* With the co-operation of L. D. Kretalova.

TABLE 1. Composition and Characteristics of Alumino-Chrome Catalysts

Sample number	Composition, mol. %		Final pH value at precipitation	AKh-450		AKh-600		AKh-1000			
	Cr ₂ O ₃	Al ₂ O ₃		Water loss on ignition, wt. %	Phase-composition	Water loss on ignition, wt. %	Phase-composition	Lattice parameters		Lattice parameters	
								γ-Al ₂ O ₃	α-Cr ₂ O ₃		γ-Al ₂ O ₃
1	—	100	6,8	3,4	α-Al ₂ O ₃	0,9	α-Al ₂ O ₃	7,80	—	δ-Al ₂ O ₃	—
2	1	99	7,6	3,95	α-Al ₂ O ₃	1,2	γ-Al ₂ O ₃	—	—	δ-Al ₂ O ₃	—
3	3	97	6,4	4,02	γ-Al ₂ O ₃	1,5	γ-Al ₂ O ₃	—	—	—	—
4	3	97	7,6	4,9	γ-Al ₂ O ₃	2,1	γ-Al ₂ O ₃	—	—	δ-Al ₂ O ₃	—
5	5	95	7,1	4,23	γ-Al ₂ O ₃	2,0	γ-Al ₂ O ₃	7,81	—	δ-Al ₂ O ₃	—
6	10	90	7,0	5,0	γ-Al ₂ O ₃	3,1	γ-Al ₂ O ₃	7,85	—	γ-Al ₂ O ₃	—
7	15	85	7,5	3,8	γ-Al ₂ O ₃	2,9	γ-Al ₂ O ₃	—	—	γ-Al ₂ O ₃ or δ-Al ₂ O ₃	—
8	15	85	6,7	6,11	γ-Al ₂ O ₃	3,4	γ-Al ₂ O ₃	7,89	—	α-Cr ₂ O ₃	—
9	25	75	7,4	6,15	γ-Al ₂ O ₃	2,0	{ γ-Al ₂ O ₃ α-Cr ₂ O ₃	7,90	5,24	{ γ-Al ₂ O ₃ α-Cr ₂ O ₃	5,23
10	50	50	6,8	2,93	{ α-Cr ₂ O ₃ γ-Al ₂ O ₃	1,5	α-Cr ₂ O ₃	—	5,25	{ γ-Al ₂ O ₃ α-Cr ₂ O ₃	5,22
11	75	25	7,4	2,42	—	1,5	α-Cr ₂ O ₃	—	5,29	α-Cr ₂ O ₃	5,26
12	90	10	6,8	1,2	α-Cr ₂ O ₃	1,7	α-Cr ₂ O ₃	—	5,30	α-Cr ₂ O ₃	5,30
13	100	—	8,8	1,0	α-Cr ₂ O ₃	1,2	α-Cr ₂ O ₃	—	5,30	—	—
14	100	—	7,0	1,1	α-Cr ₂ O ₃	1,0	α-Cr ₂ O ₃	—	5,31	α-Cr ₂ O ₃	5,31
15	100	—	8,0	1,4	α-Cr ₂ O ₃	1,6	—	—	—	—	—

TABLE 2. Texture of Alumino-Chrome Catalysts.

Catalyst	S, m ² /g		V, cm ³ /g		r_m , Å		$r_{av} = \frac{2V}{S}$, Å	
	AKh 450	AKh 600	AKh 450	AKh 600	AKh 450	AKh 600	AKh 450	AKh 600
Al ₂ O ₃	200	190	0,260	0,256	18	22	26	27
1%—I	282	204	0,278	0,270	25	32	20	26,5
3%—I	217	221	0,201	0,224	21	18,5	24	20
3%—II	260	256	0,202	0,212	17	15,5	22	16,5
5%	309	297	0,285	0,264	26	25	18,5	18
10%	288	312	0,222	0,248	18	20	15,5	16
15%—I	298	255	0,330	0,301	23	25	22	23,5
15%—II	284	320	0,209	0,230	16	16	15	14
25%	261	241	0,242	0,225	18	21	19	18,5
50%	240	142	0,188	0,165	15	20	15,5	23
75%	103*	66	0,213	0,200	37	38	41	61
90%	32*	28	0,209	0,203	105	115	130	145
Cr ₂ O ₃ —I	20*	29	—	—	(500)	(500)	—	—
Cr ₂ O ₃ —II	16*	—	0,153	—	160	—	190	—
Cr ₂ O ₃ —III	21*	14*	0,228	0,214	130	300	220	350

* After operation.

RESULTS

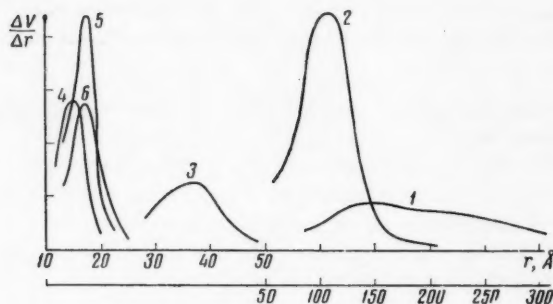


Fig. 2. Curves of the distribution of pore volume according to radius. 1) Cr₂O₃—II; 2) 90% Cr₂O₃; 3) 75% Cr₂O₃; 4) 50% Cr₂O₃; 5) 25% Cr₂O₃; 6) 10% Cr₂O₃.

with increase in temperature, and also through the progressive removal of residual water, which facilitates the sintering process. In general these effects may be expressed by saying that, in the series AKh-450, the rhombohedral phase only arises when the chromium-III oxide content is at least 50 mol.%, while in the series AKh-600 and AKh-1000 respectively, the amounts of chromium-III oxide required diminish to 25 mol.% and 15 mol.%. This latter circumstance shows the nonhomogeneity of the catalysts, since homogeneous catalysts containing 15 mol.% of chromium-III oxide cannot show the crystalline rhombohedral phase, because of the negligible excess of the oxide content in this catalyst compared with its concentration in the saturated solid solution [1], and because of the mutual protection of the phases from crystallization, which is fundamentally to be ascribed to the corundum phase, present in very small quantity. Apparently, in the series AKh-450 and AKh-600 up, the concentrations indicated above, at which according to the x-ray data the rhombohedral phase arises, there is undoubtedly formed a phase rich in chromium-III oxide to a certain extent in the actual precipitation process. This phase is formed at moderate chromium-III oxide concentrations in the catalysts, and appears either in the amorphous state, or in such a highly disperse condition that it cannot be discovered by phase analysis. At a temperature of 1000°, however, sintering occurs so intensively that this phase is crystallized even at low concentration in the catalyst. The behavior of the chromium-III oxide in the catalysts investigated by us confirms in general the observation of Visser [9] that alumina makes possible the maintenance of chromium-III oxide in the amorphous state.

Transferring our attention to the condition discovered in the mixed catalyst phases, we observe that opinions on this have been formed on the basis of measurements of the parameters of the crystalline lattices. The parameter

of the lattice of the cubic phase increases, for example, from 7.80 Å in the AKh-600 series for pure alumina, to 7.90 Å for a catalyst containing 25 mol.% of chromium-III oxide, while the γ -alumina type structure is maintained (the defective spinel structure). Thus, in the mixed catalysts AKh-450 and AKh-600, the cubic phase is a solid solution of chromium-III oxide in alumina. On the other hand, the lattice parameter of the rhombohedral phase diminishes with increase in the alumina concentration, from 5.31 Å to 5.23 Å as the concentration rises from 0 to 75 mol.%, because of the fact that the radius of the aluminum ion is less than that of the chromium ion. This change in the lattice parameter in its turn indicates that the rhombohedral phase in the mixed catalysts corresponds to a solid solution of alumina in chromium-III oxide. The comparatively slight change in the lattice parameter is explained by the small difference between the radii of the ions Al^{3+} and Cr^{3+} . Thus, with reference to the chemical nature of the phases discovered by us, there is no divergence from the views published by Davis and his colleagues [1], but a difference does exist in the crystallographic characteristics of phases rich in alumina. We have been unable to discover the η -phase, the chief distinguishing sign of which, according to Davis, is the presence on the x-ray diagrams of reflexions with $d=2.55$ Å; and phase analysis even with the use of molybdenum radiation has shown the presence of the γ -phase for the solid solution of chromium-III oxide in alumina.

In none of the catalysts have hydroxides of the metals been found by phase analysis, since these would be present in the catalysts only in the form of surface compounds, and not in the bulk. It should be remarked that in catalysts which have not yet been used in a catalytic process, though they are indicated in Table 1, there is plain evidence of the presence of some chromates. The color of the catalysts would itself give evidence of this. These, however, have also not been found in the form of crystalline phases. These compounds are easily decomposed by being heated in a high vacuum, and in a reducing atmosphere in the course of the decomposition of alcohol at 245-350°. In concluding our consideration of the results of phase analysis, we may note that in the cases we have considered (catalysts with 3, 15 and 100 mol.% chromium-III oxide), the phase composition was independent of the ultimate precipitation pH.

The data we have obtained permit us to state that chromium-III oxide exerts a stabilizing effect on γ -alumina in which it is dissolved. Thus, in cases when pure alumina forms the χ -phase, in the presence of chromium-III oxide the γ -phase is formed, as can be seen from the data in Table 1. More than this, in the temperature range in which pure alumina forms the δ -phase, chromium oxide makes the spinel γ -phase quite stable (Table 1, AKh-1000 with 10-25 mol.% chromium-III oxide). It is possible that this stabilization of the spinel structure is the result of the formation of a solid solution of chromium-III oxide in γ -alumina, since chromium-III oxide itself, if it does form phases differing from α -chromia (γ - or η -), does so only with great difficulty.

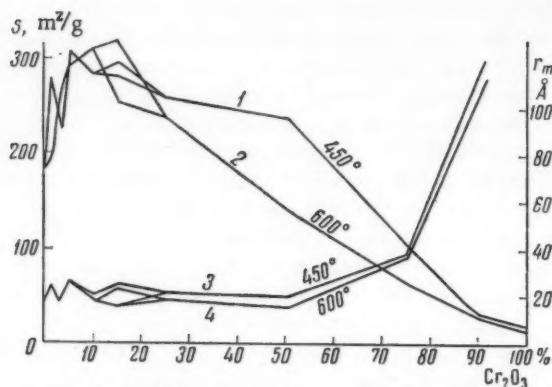


Fig. 3. Relationship between the size of the specific surface (1,2) and pore radius (3,4), and the composition of alumino-chrome catalysts ignited at 450° and 600°.

It is clearly seen from the data of Table 2 and Fig. 3 that S increases from 200 m^2/g with pure alumina to 300-320 m^2/g with catalysts containing 5-15% chromia; this is clearly to be attributed to the "mutual protective effect from crystallization", or the mutual dispersing effect of the components. Further increase in the chromium oxide content in the catalyst causes a reduction in S which increases with the percent of chromium-III oxide, until it reaches

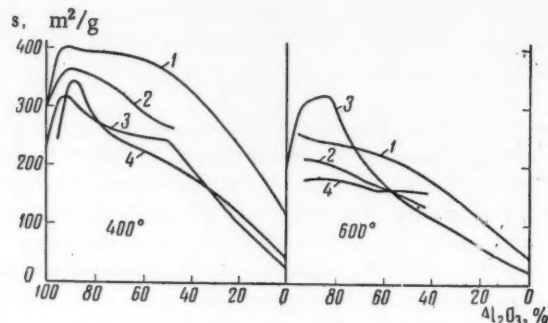


Fig. 4. Effect of ignition temperature and composition of binary catalysts based on alumina on the value of the specific surface. 1) $Al_2O_3-ZrO_2$; 2) $Al_2O_3-Fe_2O_3$; 3) $Al_2O_3-Cr_2O_3$; 4) Al_2O_3-NiC .

The magnitudes of the specific surface S change greatly with the composition of the catalyst. It is

15-20 m²/g in the pure chromium oxide. The maxima in the curves of distribution of pore volume against radius lies within the limits 15-20 Å if the chromium-III oxide content does not exceed 50 mol.%. Further increase in the content of this causes this maximum to shift to the region 105-115 Å at 90% oxide. It has not been possible to determine accurately the position of the maximum for the pure chromium oxide: either the pore radii are very large (up to 500 Å), or the chromium-III oxide is nonporous, and capillary condensation takes place in the spaces between the particles. It should be noted that the specific volume of the catalyst pores also changes considerably with the composition, and passes through a minimum at 50% chromium-III oxide. Change in the ignition temperature from 450° to 600° has little effect on the size of surface or on the porous structure of AKh catalysts. In general the AKh-600 catalysts have a smaller value for the specific surface and a larger pore radius than the corresponding AKh-450 catalysts. In the majority of cases, however, this difference is small. The reverse relationship has also been observed (for catalysts with 10 and 15% of Cr_2O_3), which must be due to chance factors. The value of the precipitation pH for repeated preparation of samples of the same composition varied within comparatively narrow limits. However, a considerable difference in the values of S for variation in the pH at precipitation was observed with Cr_2O_3 I and III, and with AKh-15 - I and II ignited at 600°. This difference was not found in the AKh-450 series.

As we have already observed in the experimental part, the texture of the preparation investigated, after catalytic experiments on the decomposition of isopropyl alcohol at 245-350°, did not undergo any change compared with the initial property. The following three conclusions can be drawn from this in relation to the catalysts studied: 1) reduction of chromium-VI compounds, which are formed in the catalysts as a result of their thermal treatment in air when the hydroxides are converted to oxides, has no effect on their texture; 2) under the conditions under which the catalytic process is carried out, neither sintering nor disaggregation of the catalysts takes place to an appreciable extent; and 3) carbon deposition does not take place on the catalyst surfaces in the course of the reaction.

Since catalytic processes are rarely carried out at temperatures higher than 600°, it is appropriate to determine the thermal stability of the catalysts near such temperatures. Since we have assembled corresponding data for the texture of a variety of binary catalysts based on alumina (Al_2O_3 -NiO [10], Al_2O_3 - Fe_2O_3 [11] and Al_2O_3 - ZrO_2 [12]), prepared by simultaneous precipitation by approximately the same method, and treated in the same way with respect to the duration of thermal treatment at 400° and 600°, it is possible to compare the thermal stability of binary catalysts of different chemical composition, and their change with change in the concentration of the components. This is done in Fig. 4, which shows that at 400° all the curves for the change of S with composition have a maximum at 5-15% of the second component. This maximum is particularly strongly expressed with alumina-nickel oxide and alumina-chromium-III oxide, showing in these cases mutual protection of the components from crystallization. After ignition at 600° this maximum disappears or is weakened for all the cases shown in Fig. 4 except that of alumina-chromium-III oxide. Thus the alumino-chrome catalysts within the temperature range studied for ignition show the greatest thermal stability from the point of view of their texture.

SUMMARY

1. Simultaneous precipitation by ammonia at a final pH of 6.4 - 7.6 of alumina-chrome catalysts containing up to 25% chromium-III oxide, gives products consisting of a solid solution of their components with a defective spinel structure (γ -phase). For higher chromia concentrations there arises a corundum (rhombohedral) phase consisting of a solid solution of alumina in the chromium oxide.
2. Neither γ - Cr_2O_3 nor η - Cr_2O_3 is observed by phase analysis of the catalysts.
3. The effect of composition and temperature of ignition on the texture of the alumino-chrome catalysts has been studied.
4. According to data on the texture of binary catalysts (alumina with chromium-III oxide, nickel oxide, ferric oxide and zirconium-IV oxide), it has been found that the alumina-chromium-III oxide system possesses the greatest thermal stability.
5. It has been shown that there is considerable effect of precipitation pH on the texture of alumino-chrome catalysts.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ON THE CATALYTIC DECOMPOSITION OF ETHYLBENZENE HYDROPEROXIDE

A. G. Korsun, V. Ya. Shlyapintokh and N. M. Émanuel'

The Institute of Chemical Physics, Academy of Sciences, USSR

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Systems composed of a salt of a metal of variable valence and a peroxide are widely used for the catalysis of the oxidation of hydrocarbons and for the initiation of radical polymerization reactions. The mechanism of the action of such systems is that they generate free radicals in solution and thus increase the rate of initiation of chains. During the process of the oxidation of hydrocarbons, the salt catalysts are altered. During the reaction the valence of the metal changes, the products of the reaction form complexes with the metal salt, and in a number of cases the metal salt falls out in the sediment [1,2]. The catalyst can participate not only in the initiation of chains but also in reactions of chain-termination and, apparently, in reactions of chain-propagation [3,4]. The reaction kinetics are made extremely complicated by such large changes of properties and by the variety of functions of the catalyst, and the establishment of a mechanism for catalytic action of these salts is made more difficult. Therefore, for solution of the latter general problem it appeared expedient to us to divide the catalytic oxidation reaction of hydrocarbons into steps and to study each of these steps individually. The present work is devoted to an investigation of one of the most important steps of the catalytic oxidation reaction, namely: the interaction between a hydroperoxide and a metal salt of variable valence.

EXPERIMENTAL

Copper stearate was obtained by adding a 22% solution of copper sulfate (C.P.) to an equivalent quantity of a 1% solution of sodium stearate heated to 70°. The precipitate of copper stearate was filtered off, washed several times on the filter with hot water and dried to constant weight in a desiccator over concentrated sulfuric acid. Chlorobenzene (Pure) was shaken with several portion of 5% oleum. When the acid layer ceased to become colored, the chlorobenzene was washed with distilled water. Peroxidic compounds were removed by treatment with a solution with sodium bisulfite, and the excess of reducer was oxidized with basic potassium permanganate solution which was removed with water. After this, the chlorobenzene was dried over metallic sodium and was distilled in vacuo at 50-60°. Pure ethylbenzene was purified in the same way as the chlorobenzene and distilled at 40°. The hydroperoxide of ethylbenzene was obtained by oxidation of the ethylbenzene with atmospheric oxygen at 120°; it was isolated by the method described in the monograph of Ivanov [5]; it was dissolved in chlorobenzene, and was dried over anhydrous magnesium sulfate. Pure acetophenone was purified by fractional freezing. The benzyl alcohol used was labeled "pure." Separate experiments were carried out with alcohol which was purified by boiling with 2,4-dinitrophenylhydrazine and twice distilling in vacuo. Diphenylpicrylhydrazyl was obtained from the Institute of Organic Chemistry, AN USSR; its molar adsorption coefficient in the green maximum was 12,000, which is in agreement with the data from the literature [6]. No purification of the diphenylpicrylhydrazyl was made. Nitrogen from a cylinder was freed of oxygen with an ammoniacal solution of cuprous chloride. The ammonia was absorbed in traps containing 50% sulfuric acid; for removal of water, the nitrogen was passed through a spiral cooled with liquid nitrogen. The solutions of hydroperoxide and copper stearate were bubbled with nitrogen at room temperature for 15 min to remove oxygen.

The reactions were carried out in the vessel depicted in Fig. 1. The copper stearate solution was placed in vessel A, the hydroperoxide solution in vessel B. A current of nitrogen was introduced through tube C and both solutions were freed of oxygen. After this the vessel was immersed in a thermostat and heated to the given temperature. The stream of nitrogen was then directed into vessel B and the peroxide solution was transferred to vessel A under this pressure, where in less than 5 sec it was mixed with the stearate solution.

Samples of the reaction mixture were forced into the bulb D by increasing the pressure of nitrogen in vessel A;

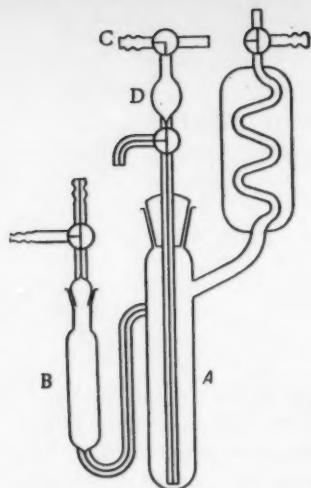


Fig. 1. Vessel for the kinetic experiments.

greater and could reach 100%. To decrease the error, every experiment was repeated several times and the average values were used.

The kinetics of the catalytic decomposition of hydroperoxide. The catalytic decomposition of the hydroperoxide of ethylbenzene was carried out in the inert solvent chlorobenzene in the temperature interval 60–110°. The lower temperature boundary of the interval was determined by the solubility of the catalyst - copper stearate, the higher, by the boiling point of the solvent (132°). The initial concentration of the hydroperoxide was varied from 0.3–0.03M, and of the copper stearate from $4 \cdot 10^{-3}$ – $0.2 \cdot 10^{-3}$ M.

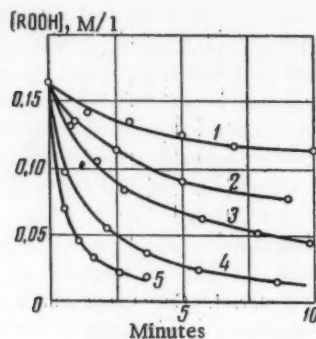


Fig. 2. Kinetic curves of the decomposition of ethylbenzene hydroperoxide (0.165M) at various concentrations of CuSt_2 at 100°. Concentrations of CuSt_2 in moles per liter: 1) $0.228 \cdot 10^{-3}$; 2) $0.457 \cdot 10^{-3}$; 3) $0.914 \cdot 10^{-3}$; 4) $2.28 \cdot 10^{-3}$; 5) $4.44 \cdot 10^{-3}$.

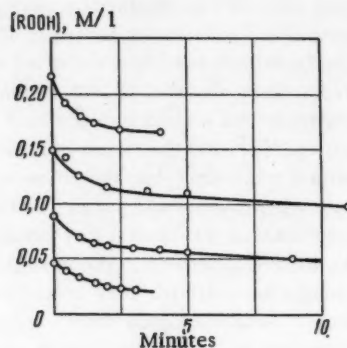


Fig. 3. Kinetic curves of the decomposition of ethylbenzene hydroperoxide for various initial concentrations of the hydroperoxide; $t = 70^\circ$; $(\text{CuSt}_2) = 2.36 \cdot 10^{-3}$ M.

The kinetic curves of the catalytic decomposition of hydroperoxide at various concentrations of copper stearate and hydroperoxide, and at different temperatures are given in Figs. 2, 3, and 4. From the graphs one can see that the hydroperoxide is not all decomposed. The absolute quantity of decomposed hydroperoxide is increased by increased concentration of the catalyst and of the hydroperoxide, and also by an increase of the temperature. These facts show that the catalytic decomposition reaction is complex. In order to exclude as much as possible the influence of secondary processes, we took as the kinetic characteristic of the reaction the initial rate of decomposition w_0 .

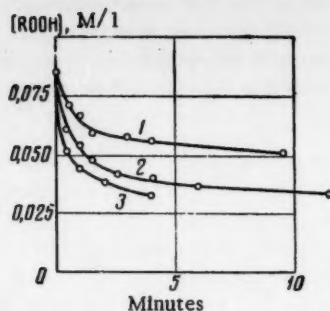


Fig. 4. The kinetic curves of the decomposition of ethylbenzene hydroperoxide at different temperatures: $(\text{CuSt}_2) = 2.28 \cdot 10^{-3} \text{ M}$; $[\text{ROOH}] = 0.085 \text{ M}$; 1) 70° ; 2) 80° ; 3) 90° .

In Figs. 5 and 6 are depicted the dependence of the initial rate of decomposition w_0 on the concentrations of copper stearate $(\text{CuSt}_2)_0$ and of the hydroperoxide $(\text{ROOH})_0$. Since the dependence of w_0 on the concentrations of reagents is linear, an empirical expression for the initial rate has the form

$$w_0 = k[\text{ROOH}]_0 \cdot [\text{CuSt}_2]_0 \quad (1)$$

The rate constant k changes with the temperature according to the law of Arrhenius. We carried out the experiments with two specimens of the hydroperoxide. The activation energies and the rate constants for both specimens were nearly the same. From the experimental dependence of the initial rate of the reaction on the concentrations of the reagent and on the temperature, the over-all rate constant for the catalytic decomposition of the hydroperoxide is

$$k = 1.4 \cdot 10^{-11} \exp \left(- \frac{15800}{RT} \right) \text{ cm}^3/\text{sec}$$

For the other specimen of hydroperoxide

$$k = 2.8 \cdot 10^{-11} \exp \left(- \frac{15500}{RT} \right) \text{ cm}^3/\text{sec}$$

The alteration of the catalyst during the course of the reaction. The bimolecular law established for the decomposition is justified only for the initial stage of the reaction and does not describe the whole kinetic curve of decomposition. As was observed above, these deviations are connected with secondary processes occurring in the system. The most important of the secondary processes is undoubtedly the alteration of the catalyst which is shown by the visible change of the color of the solution. When solutions of the hydroperoxide and of copper stearate are mixed at temperatures of $90-100^\circ$, the color momentarily changes from a bluish-green to green. The green color then gradually weakens and the color of the solution changes to yellow.

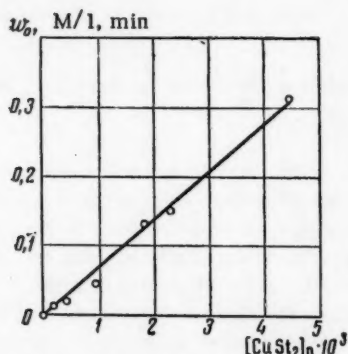


Fig. 5. The dependence of the initial rate of the decomposition of ethylbenzene hydroperoxide on the concentration of CuSt_2 at 100° ; $[\text{ROOH}] = 0.165 \text{ M}$.

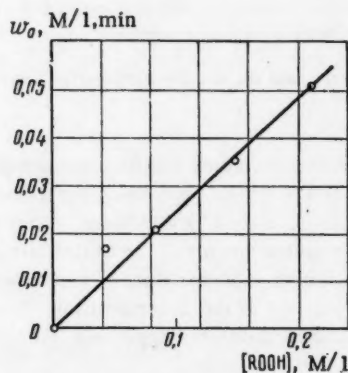


Fig. 6. The dependence of the initial rate of decomposition of ethylbenzene hydroperoxide on the initial concentration of hydroperoxide at 70° ; $[\text{CuSt}_2] = 2.36 \cdot 10^{-3} \text{ M}$.

For the purpose of explaining the observed changes of color of the solution, absorption spectra were made of copper stearate in chlorobenzene, and also of copper stearate in the presence of the products of the reaction, since one could expect that the polar molecules of the products - alcohol and ketone - will form complex compounds with the copper stearate. A solution of divalent copper stearate possesses a characteristic maximum in the region $670-680 \text{ m}\mu$. The position of the maximum is not changed for the complex compounds of copper with the products of the reaction, but its intensity increases. As a result of this change in the spectrum, the solution becomes green. The observed momentary change of color to green when the solutions of hydroperoxide and copper stearate are blended is obviously connected with the formation of peroxidic complexes and complexes with the products.

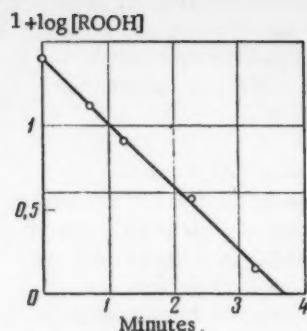


Fig. 7. The kinetics of the decomposition of ethylbenzene hydroperoxide (0.0105M) in the presence of a comparable concentration of CuSt_2 (0.0228 M) at 60° . The concentration of the hydroperoxide is expressed in conventional units.

After the formation of the hydroperoxide complex, the change in composition of the catalyst continues: the divalent copper gradually is converted to monovalent. The change of valence can be followed by the decrease of the optical density of the solution in the region of the red maximum since the stearate of monovalent copper is a colorless compound.

It was not possible to follow quantitatively the kinetics of the valence change, because several colored forms of the salt of divalent copper are present in the solution. During the course of the decomposition the solution gradually becomes yellow. Special experiments showed that there is no copper in the yellow compound which is formed. Apparently the yellow product is a polymeric compound.

It was shown above that at small values of the ratio of the concentration of copper stearate to the concentration of hydroperoxide the decomposition reaction does not proceed to completion. The experimentally observed correspondence between the fall of the rate of the reaction and the conversion of divalent copper into monovalent led us to the conclusion that the cessation of the reaction is connected with the destruction of the catalyst. This conclusion was directly confirmed by experiment: a new portion of hydroperoxide introduced into a system in which the reaction had already ceased was not decomposed, but the addition of a new portion of catalyst led to a renewal of the decomposition reaction. In proportion to the increase in the ratio of the concentration of copper stearate to the concentration of hydroperoxide, the kinetics of the decomposition are influenced to a smaller

extent by the destruction of the catalyst, and the extent of the reaction increases. For $2.28 \cdot 10^{-3}$ M copper stearate and $2.25 \cdot 10^{-2}$ hydroperoxide, i. e., at a ten-fold excess of hydroperoxide, the decomposition proceeds to completion even at the lowest temperature (60°). For a 1 : 1 ratio of the concentration of copper stearate and hydroperoxide [CuSt_2] = $2.28 \cdot 10^{-3}$ M and hydroperoxide = $2.25 \cdot 10^{-2}$ M, the concentration of hydroperoxide changes during the reaction strictly according to the first order law (Fig. 7). This shows the constancy of the activity of the catalyst to the end of the decomposition reaction.

The kinetic law for the decomposition thus coincides with that which was established for the initial rate

$$w = k [\text{CuSt}_2]_0 [\text{ROOH}] \quad (2)$$

with the only difference being that in expression (2) there is stated not the initial, but the actual concentration of the hydroperoxide at any time. From these experiments there were obtained the following values of the rate constant for the decomposition: at 60° $k = 39$ liters/M, min; at 70° $k = 80$ liters/M, min; these coincide with the values obtained earlier from the measurements of the initial rate of the process. The activation energy $E = 16$ kcal/M obtained in experiments with high concentrations of copper stearate also coincides with the value which was determined on the basis of the initial rate of the decomposition. Thus under conditions in which the catalyst is not converted into an inactive form of a monovalent copper salt, the decomposition of the hydroperoxide goes according to a second order law to the end of the reaction.

The mechanism of the catalytic decomposition of the hydroperoxide. At small concentrations of copper stearate, when the destruction of the catalyst strongly influences the kinetics of the process, the quantity of decomposed hydroperoxide exceeds by several orders of magnitude the initial quantity of copper stearate. Two general mechanisms can explain this fact. Firstly, a catalytic mechanism in which the decomposition is realized in the act of the interaction of the hydroperoxide with the salts of divalent and monovalent copper. Secondly, a chain mechanism in which the reaction between the metallic salt and the hydroperoxide gives rise only to a chain, and the hydroperoxide decomposes basically by a chain mechanism. If the second mechanism is justified, then the rate of the decomposition must be considerably changed in the presence of a quantity of a product of the reaction, which strongly influences the rate of the non-catalyzed decomposition of hydroperoxide [7].

Experiments showed that additions of benzyl alcohol* and acetophenone in quantities which exceed by several times the concentration of the hydroperoxide practically do not influence the kinetics of the reaction, and also that the initial rate of the reaction is not influenced by the addition of ethylbenzene, although the energy of the C-H

*Benzyl alcohol was used instead of the product of the decomposition reaction - methylphenylcarbinol.

bond of the α -carbon atoms of ethylbenzene is considerably lower than the energy of the C-H bond in chlorobenzene.

This fact favors the first, catalytic mechanism of the decomposition. A direct indication of the catalytic mechanism of the decomposition is given also by the direct proportionality of the dependence of the rate of the process on the concentrations of hydroperoxide and copper stearate. If the share of the chain decomposition were significant, then in the expression for the rate of decomposition as a rule there would appear a non-linear dependence on at least one of the reagents.

In order to reach a definite conclusion as to the extent of the contribution of the chain mechanism, experiments were carried out to measure the rate of formation of radicals in the catalytic decomposition of hydroperoxide. Diphenylpicrylhydrazyl was used for this purpose. Diphenylpicrylhydrazyl is a stable free radical. Interacting with the radicals which are formed in the course of the decomposition of the hydroperoxide, it inhibits the chain reaction [8]. Through the use of diphenylpicrylhydrazyl we expected that in the catalytic decomposition reaction the rate of its transformation would be smaller or equal to the rate of decomposition of the hydroperoxide. If the rates were equal, the decomposition would be purely catalytic. If the rate of disappearance of the diphenylpicrylhydrazyl was smaller than the rate of decomposition, the reaction would have a chain character, the ratio of the rate of decomposition to the rate of disappearance being equal to the average length of the chain.

Solutions of diphenylpicrylhydrazyl are strongly colored; it is decolorized by reaction with radicals, being converted to a weakly colored substance. Therefore, the change of concentration of the diphenylpicrylhydrazyl is conveniently measured colorimetrically. In our experiments, the kinetics of decolorization were measured at a wave length of 527 m μ .

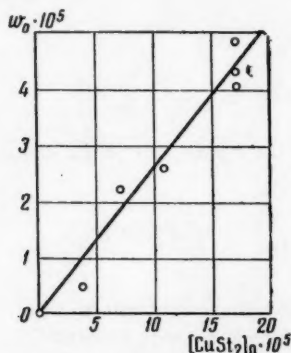


Fig. 8. The dependence of the initial rate (M/liters, min) of the disappearance of diphenylpicrylhydrazyl ($7.15 \cdot 10^{-5}$ M) on the concentration of CuSt_2 ; $[\text{ROOH}] = 10.6 \cdot 10^{-5}$ M; $t = 70^\circ$

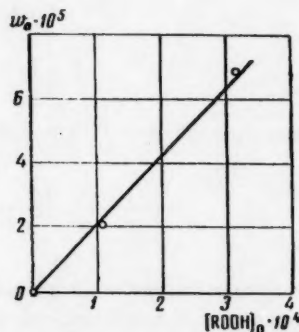


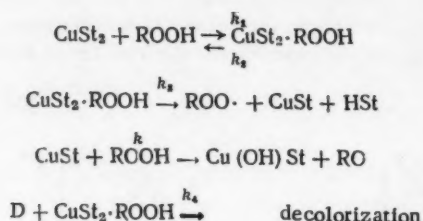
Fig. 9. The dependence of the initial rate (M/liters, min) of the disappearance of diphenylpicrylhydrazyl ($7.15 \cdot 10^{-5}$ M) on the initial concentration of hydroperoxide; $(\text{CuSt}_2)_0 = 7.15 \cdot 10^{-5}$ M; $t = 70^\circ$

The spectrum of diphenylpicrylhydrazyl dissolved in chlorobenzene is practically unchanged after several days. In the presence of hydroperoxide (concentration $5 \cdot 10^{-4}$ M) the initial rate of decolorization of the diphenylpicrylhydrazyl at 70° is $7.9 \cdot 10^{-7}$ M/liters, min, which is two orders of magnitude smaller than the rate of disappearance of diphenylpicrylhydrazyl during the catalytic decomposition of the hydroperoxide. Additions of hydroperoxide to a solution of diphenylpicrylhydrazyl in chlorobenzene do not change the absorption spectra of the solution. The spectra of mixtures of copper stearate and diphenylpicrylhydrazyl are additive. These facts show that diphenylpicrylhydrazyl does not form complexes with the reagents. Control experiments showed that in the presence of copper stearate at 70° diphenylpicrylhydrazyl is not decolorized. The initial rates which we measured were determined from the initial slopes of the curves of the decolorization of diphenylpicrylhydrazyl with an error of approximately 10%.

Experiments with different concentrations of copper stearate and hydroperoxide in the presence of diphenylpicrylhydrazyl ($7.15 \cdot 10^{-5}$ M) were carried out at 70° . The dependences of the initial rates of disappearance of the diphenylpicrylhydrazyl on the concentrations of copper stearate and hydroperoxide are depicted in Figs. 8 and 9

respectively. From the figures it is apparent that the initial rate of decolorization is linearly dependent on the concentrations of copper stearate and hydroperoxide. The rate constant of the disappearance of diphenylpicrylhydrazyl was equal to 2800 liters/M, min, while the rate constant for the decomposition of the hydroperoxide measured in the earlier experiments was at most 100 liters/M, min. In spite of the assumptions, it turned out that the rate of disappearance of the diphenylpicrylhydrazyl was almost 30 times greater than the rate of decomposition of the hydroperoxide.

This result was explained by Voevodskii, who suggested that the diphenylpicrylhydrazyl reacts in our system not only with the radicals but also with some kind of active intermediate product. Since we measured the initial rates of the reaction, this active product which is not present in the hydroperoxide or copper stearate solutions must arise within a very short time after the mixing of the solutions. This product is apparently the complex of the hydroperoxide with copper stearate. Thus the hypothesis of Voevodskii is that as a result of the formation of the complex the hydroperoxide is strongly activated, and direct reaction between the hydroperoxide in the complex and diphenylpicrylhydrazyl becomes possible. If the hydroperoxide is activated, then even the reaction of catalytic decomposition of the hydroperoxide must go basically through the peroxidic complex. On the basis of these conceptions, one can write the following scheme for the reaction of catalytic decomposition in the presence of diphenylpicrylhydrazyl



where D is diphenylpicrylhydrazyl. The initial rate of disappearance of the diphenylpicrylhydrazyl is

$$-\left(\frac{d(D)}{dt}\right)_0 = \left\{ \frac{2k_1k_3}{k_2 + k_3 + k_4(D)} + \frac{k_1k_4(D)}{k_2 + k_3 + k_4(D)} \right\} [\text{CuSt}_2]_0 [\text{ROOH}]_0$$

The over-all rate constant for the disappearance of diphenylpicrylhydrazyl is enclosed within the braces. The first term of the constant is concerned with the reactions of diphenylpicrylhydrazyl with free radicals, the second with the reaction of diphenylpicrylhydrazyl with the peroxidic complex. Expression (3) explains the experimentally observed dependence of the rate of decolorization of the diphenylpicrylhydrazyl on the initial concentrations of copper stearate and hydroperoxide.

In principle the measurement of the dependence of the overall rate constant of the disappearance of diphenylpicrylhydrazyl on its concentration should allow all of the individual rate constants of the scheme given above to be determined. In actuality one can obtain from this dependence two relations between the rate constants. Another relation is known from the experiments on the catalytic decomposition in the absence of diphenylpicrylhydrazyl. And, finally a fourth relation is known - the equilibrium constant for the reaction of the formation of the complex.

SUMMARY

1. The kinetics of the catalytic decomposition of ethylbenzene hydroperoxide has been investigated. The initial rate of the decomposition is proportional to the concentrations of the catalyst - copper stearate and of the hydroperoxide.
2. In the presence of a large excess of hydroperoxide, the catalyst is transformed during the reaction into an inactive form of monovalent copper and the reaction stops. The quantity of hydroperoxide decomposed increases with an increase of the concentrations of catalyst and of hydroperoxide, and also with an increase of the temperature.
3. Under the experimental conditions, the decomposition goes principally by a catalytic mechanism, and the chain mechanism does not play a substantial role.

4. When the reaction is carried out in the presence of an inhibitor - diphenylpicrylhydrazyl, it is observed that the rate constant for the disappearance of the inhibitor considerably exceeds the rate constant of the catalytic decomposition of the hydroperoxide.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

ON THE PROBABILITY OF SELF-INHIBITION OF COMPLEX CHAIN REACTIONS

E. T. Denisov

The Institute of Chemical Physics, Academy of Sciences USSR

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The phenomenon of self-inhibition of complex chain-reactions, for example the oxidation of hydrocarbons to which Emanuel' [1,2] first turned attention, is wide-spread. One of the causes of the self-inhibition of these reactions is the change in the composition of the radicals during the process [3-6]. In the present work, the question of the probability of the self-inhibition of complex chain reactions as a consequence of the change of the composition of the radicals is examined in the light of certain assumptions, and it is shown that this probability is very great. The change of the composition of the radicals in a complex chain reaction occurs because the intermediate products react with the free radicals and supply to the system radicals of another kind. The complication of the composition of the radicals during the reaction is reflected in its rate. We will develop a formula reflecting the change of the rate of disappearance of the starting material as a consequence of the changing composition of the radicals.

Let the intermediate products $P_1 \dots P_i \dots P_m$, be formed from the starting material RH as a result of a chain reaction; each of these furnishes its own kind of free radical; the concentration of these radicals will be designated by $n_1 \dots n_i \dots n_m$. The rate of disappearance of RH is equal to

$$v = -\frac{d[RH]}{dt} = \sum_{i=0}^m k_{i0} n_i [RH] = k_{00} [RH] n \sum \alpha_{i0} n'_i,$$

where K_{i0} is the rate constant of the reaction of the i -th radical with RH; $n'_i = n_i/n$, sp, $\alpha = k_{i0}/k_{00}$. The total concentration of free radicals n also depends on their composition. Let us assume that termination of the chains is linear and that radicals of the i -th kind disappear with rate $k'_i n_i$. In the stationery state of the reaction

$$\begin{aligned} w_i &= \sum_{i=0}^m k'_i n_i = k'_0 n \sum \beta_i n'_i; \quad \beta_i = \frac{k'_i}{k'_0}; \\ n &= w_i / k'_0 \sum \beta_i n'_i; \\ v &= \frac{k_{00} [RH] w_i}{k'_0} F; \quad F = \frac{\sum \alpha_{i0} n'_i}{\sum \beta_i n'_i}, \end{aligned}$$

where w_i is the rate of formation of the free radicals, which in degenerately branching chain reactions depends on the concentrations of the intermediate products. The function F shows by how many times the rate of the reaction is changed due only to changes of the composition of the radicals. For a second order chain termination, where the i -th and the j -th free radicals react with rate $k'_{ij} n_i n_j$, the total concentration of free radicals n is equal to

$$\begin{aligned} w_i &= 2 \sum_{i,j=0}^m k'_{ij} n_i n_j = 2k'_{00} n^2 \sum \beta_{ij} n'_i n'_j; \\ \beta_{ij} &= \frac{k'_{ij}}{k'_{00}}; \quad n = (w_i / 2k'_{00})^{1/2} (\sum \beta_{ij} n'_i n'_j)^{-1/2} \end{aligned}$$

$$v = k_{00} [\dot{R}H] \left(\frac{w_i}{2k_{00}} \right)^{1/2} F; \quad F = \frac{\sum_i \alpha_{i0} n_i}{\left(\sum_{i,j} \beta_{ij} n_i n_j \right)^{1/2}}.$$

This expression may be simplified by taking to a first approximation $\beta_{ij} = \sqrt{\beta_{ii}\beta_{jj}}$, which is equivalent to $k_{ij} = \sqrt{k_{ii}k_{jj}}$ (condition I), then

$$\sum_{i,j} \beta_{ij} n_i n_j = \left(\sum_i \sqrt{\beta_{ii}} n_i \right)^2; \quad F = \frac{\sum_{i=0}^m \alpha_{i0} n_i}{\sum_{i=0}^m \sqrt{\beta_{ii}} n_i}.$$

The problem of finding n_i in the form of a function of $[P_i]$ and α_{ij} has been solved in a general form [4] for the stationary state of the reaction and for sufficiently long chains. This dependence acquires an especially simple form if the condition is fulfilled for all the radicals [4]: $\alpha_{ij} = \alpha_{i0} \cdot \alpha_{0j}$ or $k_{ij}/k_{0j} = k_{i0}/k_{00}$ (condition II); this means that the relative difference in the activities of the radicals is maintained in the reactions with RH, $P_1 \dots P_m$. As already has been shown, equation II is fulfilled if the heats of all of the reactions of the i -th radicals with the j -th products are of the same sign, Polanyi's relation is fulfilled between the heat and the activation energy [7], and a linear dependence between the activation energy and the logarithm of the pre-exponential term is observed [8]. For liquid phase oxidation reactions all these conditions are fulfilled rather often. If condition II is observed, then $(\pi_i = \frac{[P_i]}{[RH]})$:

$$n_i = \frac{\frac{\alpha_{0i}}{\alpha_{i0}} \pi_i}{1 + \sum_{i=1}^m \frac{\alpha_{0i}}{\alpha_{i0}} \pi_i}; \quad F = \frac{\sum_{i=0}^m \alpha_{0i} \pi_i}{\sum_{i=0}^m a_i \alpha_{0i} \pi_i} \quad (III)$$

$$a_i = \begin{cases} \frac{\beta_i}{\alpha_{i0}} & \text{for linear chain termination} \\ \frac{1}{\sqrt{\beta_{ii}}} & \text{for second order chain termination and condition I} \end{cases}$$

Radicals of the i -th kind will accelerate the reaction if $a_i < 1$ and decelerate it if $a_i > 1$. If all $a_i = 1$, then $F = 1$ and the changing composition of the radicals will not influence the rate of the reaction.

Let us examine a typical case, where the products P_i are sequentially converted one into the other by a chain path.



During the reaction the concentrations of these products strive to reach their kinetic equilibrium limits: $\pi_i \rightarrow \pi_{ip}$. If condition II is satisfied $\pi_{ip} = \frac{1}{\alpha_{0i}}$ [5], and in a branching reaction, where $\pi_i \approx \pi_{ip}$

$$F \approx F^* = \frac{1+m}{1 + \sum_{i=1}^m a_i} \quad (IV)$$

F^* shows by how many times the rate of the branching chain reaction has changed as a consequence of changes of the composition of the radicals; it possesses the interesting feature that

$$\lim_{a_i \rightarrow 0} F^* = 1 + m; \quad \lim_{a_i \rightarrow \infty} F^* = 0,$$

i. e., the appearance of radicals with very small values of a_i cannot accelerate the reaction more than $(1 + m)$ times, while radicals with a_i greater than unity can strongly decelerate it by any amount. It is natural to pose the question: is this feature of the mechanism of complex chain reactions the main cause of their self-inhibition? In order to answer this question we will use the apparatus of the theory of probability. We will examine a great number (majority) of complex chain reactions with sequential conversion of the intermediate products. Conditions I (if the chain termination is second order) and II are fulfilled for all of the reactions. Let us assume that the probability of the appearance in the reaction of radicals with $a_i \leq 1$ and with $a_i > 1$ is the same: $p(a_i \leq 1) = p(a_i > 1) = 1/2$. Such an assumption brings out most clearly the role of the influence of the complex composition of the radicals on the rate of the reaction as the main cause of the self-inhibition of chain reactions. Self-inhibition of the reaction we will define as the fulfillment of the inequality: $F^* < 1$. The problem lies then in finding the probability $P(F^* < 1)$.

We will simplify our problem by assuming that the random quantity a_i can with equal probability take one of two values: a or $1/a$ ($a > 1$). One can consider a as the mathematical expectation of all $a_i > 1$: $M(a_i > 1) = \sum_{a_i > 1} p_i a_i$, and $1/a$ as $M(a_i < 1)$. If in a given reaction of m kinds of free radicals, l have the value a and $m-l$ the value $1/a$, then, in agreement with formula (IV)

$$F_l^* = \frac{1 + m}{1 + al + (m-l)1/a}. \quad (V)$$

The probability of the occurrence F_l^* , in agreement with the theorem of independent experiments of the theory of probability, is equal [9] to

$$p(F_l^*) = \frac{1}{2^m} \frac{m!}{l!(m-l)!}. \quad (VI)$$

Since according to the assumption, a_i can take on only the discrete values a or $1/a$, so also F_l^* can take on only definite discrete values. The graphic characteristic of the distribution of the probability of the random value F^* is a polygon. This polygon is shown in Fig. 1 for the particular case when $a=5$, $m=9$. It is clearly apparent that values of $F^* < 1$ are most probable. Using formulas (V) and (VI) it is possible to calculate the probability of the self-inhibition of reactions with a given number of intermediate products m for various a when, as before, $a_i = a$ or $1/a$

$$P(F^* < 1) = \sum P(F_l^* < 1) \quad (VII)$$

Only p for $F_l^* < 1$ enter the summation. In Fig. 2 are shown the results of such a calculation performed for two values of a ($a=2$ and $a=5$). As is apparent from Fig. 2, the probability of the self-inhibition of a complex chain reaction is higher the greater m , i. e., the more complex the mixture of radicals, and the greater a , (the greater the range of variation of a_i). For sufficiently large values of m and a ($m \geq 4$, $a \geq 5$), the probability of self-inhibition is very large—0.9 and higher.

One can judge how great the self-inhibition will be in the majority of cases from the magnitude of the mathematical expectation F^*

$$MF^* = \sum_{l=0}^m p(F_l^*) \cdot F_l^* = \frac{1+m}{2^m} \sum_{l=0}^m \left[1 + \frac{m}{a} - \left(a - 1/a \right) l \right]^{-1} \frac{m!}{l!(m-l)!} \quad (VIII)$$

The change of MF^* as a function of m is shown in Fig. 3: the greater m , the smaller MF^* , i. e., the more

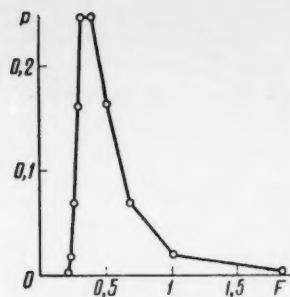


Fig. 1. The polygon of the distribution of the probabilities of the random quantity F^* calculated according to formulas (V) and (VI) for $a=5$ and $m=9$.

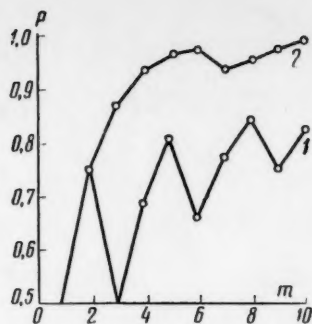


Fig. 2. The probability of the self-inhibition of reactions, $P(F^* < 1)$, as a function of the number of products \underline{m} : 1) for $a=2$; 2) for $a=5$.



Fig. 3. The mathematical expectation F^* as a function of \underline{m} for $a=10$, formula (VIII)

probable is a greater self-inhibition. In this way, a simple calculation made under the assumption of an equal probability for the formation of radicals with $a_i > 1$ and $a_i < 1$ leads to a conclusion about the high probability of the self-inhibition of complex chain reactions caused by changes of the composition of the radicals.

The foregoing calculations were made under the assumption that a_i can take on one of two discrete values. Much closer to real conditions is the assumption that a_i can take on any value between $a_i \text{ min}$ and $a_i \text{ max}$, so that $P(a_i > 1) = P(a_i < 1) = \frac{1}{2}$. We will seek the probability of the self-inhibition of the reaction $P(F^* < 1)$. For the solution of this problem we will change the random variable from a_i to $x_i = \log a_i$. Let us assume that $a_i \text{ min} = 1/a_i \text{ max}$ and take: $\lg a_i \text{ max} = b$, $\lg a_i \text{ min} = -b$. The change of a_i over the interval $[a_i \text{ min}, a_i \text{ max}]$ corresponds to the change of x_i over the interval $[-b, b]$. We will further assume that all values of x_i over the interval $[-b, b]$ are equally probable, in other words that the probability that a given x_i lies between x_i and $x_i + \Delta x_i$ is equal to $\Delta x_i / 2b$. It is obvious that $P(x_i < 0) = P(x_i > 0) = \frac{1}{2}$. We will take $m=2$ and find the probability that $F^* < 1$. The region of values taken by x_1 (designated by x) and by x_2 (designated by y) is represented by a square on the plane x, y with sides equal to $2b$ (Fig. 4). The probability that $\log a_1$ lies between x and $x + dx$ and the \log of a_2 between y and $y + dy$ is equal to $dx dy / 4b^2$. Finding $P(F^* < 1)$ is reduced to finding the region of values x and y for which $F^* < 1$. In agreement with formula (IV)

$$F^* = \frac{3}{1 + 10^x + 10^y}$$

The line which divides the region of values x, y where $F^* > 1$ from the region of values x, y , where $F^* < 1$ has the form

$$y = \lg(2 - 10^x) \quad (\text{IX})$$

In Fig. 4. is shown the line $y = \lg(2 - 10^x)$ and the region of values x and y for which F^* is < 1 . For $m=2$, $P(F^* < 1) = 0.69$. If we consider the case where $m=3$, then the region of values in which x_1, x_2 , and x_3 lie will be represented by a cube in three-dimensional space. In the general case of \underline{m} kinds of free radicals, there will be a "cube" in a space of \underline{m} dimensions. We will develop and approximate formula for $P(F^* < 1)$ for any \underline{m} . Notice that in the case where $m=2$, the curve $y = \lg(2 - 10^x)$ has 2 asymptotes: $x = \lg 2$ and $y = \lg 2$, but the area, $(b + \lg 2)^2$ which these asymptotes cut from the x, y square is somewhat greater than the area cut out by the line $y = \lg(2 - 10^x)$, therefore $P(F^* < 1) > 1 - \frac{(b + \lg 2)^2}{2b^2}$. In the case where $m=3$, the surface for which $F^* = 1$ has the asymptotic surface: $x_1 = \lg 3, x_2 = \lg 3, x_3 = \lg 3$, parallel to the coordinate surfaces: $x_2 O x_3, x_1 O x_3$, and $x_1 O x_2$. These asymptotic surfaces cut from the cube of values x_1, x_2 , and x_3 with volume $(2b)^3$ a smaller cube of volume $(b + \lg 3)^3$ and

$$P(F^* < 1) > 1 - \left(\frac{b + \lg 3}{2b} \right)^3 \quad (\text{X})$$

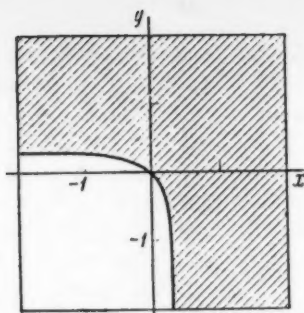


Fig. 4. Region of values for \underline{x} and \underline{y} for which $F^* < 1$ (crosshatched area) for $b = 2$. Curves, points for which $F^* = 1$, are plotted according to formula (ix).

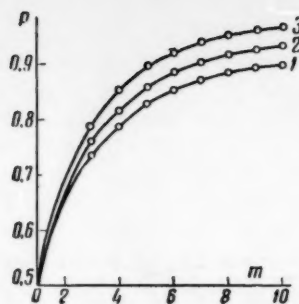


Fig. 5. The probability of self-inhibition of reactions as a function of \underline{m} , constructed according to formula (XI) for the different values: 1) $b = 1.74$; 2) $b = 2$; 3) $b = 2.6$.

For the general case of \underline{m} products, the inequality

$$P(F^* < 1) > 1 - \left(\frac{b + \lg m}{2b} \right)^m \quad (XI)$$

is obtained. This formula is a good approximation for the condition: $b > \log m$. It is possible to show that the upper boundary of $P(F^* < 1)$ is $1 - \frac{1}{2m}$:

$$1 - \frac{1}{2m} > P(F^* < 1) > 1 - \left(\frac{b + \lg m}{2b} \right)^m.$$

The region of variation of a_i can encompass several orders of magnitude. In liquid phase oxidation reactions k_{10}/k_{00} can change in order by at least one in either direction. The region of variation of the rate constants of a second order chain termination encompasses four orders: from 10^4 to 10^8 liters/M, sec, and β_{ii} can change as a minimum by two orders in either direction. Consequently

$$\begin{aligned} a_{i\max} &= \frac{\sqrt{\beta_{ii}}}{\alpha_{i0}} = \frac{\sqrt{100}}{0.1} = 100; \quad a_{i\min} = \frac{\sqrt{0.01}}{10} = \\ &= 0.01; \quad b = \lg(a_{i\max}) = 2. \end{aligned}$$

Cases are possible for which $b = 3$. The dependence of $P(F^* < 1)$ on \underline{m} for different values of \underline{b} is shown in Fig. 5. From Fig. 5 it is apparent that the larger \underline{m} (the more complex the composition of the radicals in the branching reaction) and the larger \underline{b} (the region of possible values of a_i), the greater the probability of self-inhibition of the reaction, which beginning with $m = 4$ is greater than 0.8.

Note that several simplifications made during the calculation were such that they could only decrease $P(F^* < 1)$, and the calculated values of $P(F^* < 1)$ represent a trustworthy lower limit to the probability of the self-inhibition of complex chain reactions. For the development of the formula for F^* , it was assumed that in the expression $\beta_{ij} = \Phi \sqrt{\beta_{ii} \beta_{jj}}$ $\Phi = 1$. From experience, it is known that in the majority of cases $\Phi > 1$ and is equal to 2-4. Therefore in reality F^* is smaller than one would conclude from formula (IV), and $P(F^* < 1)$ is greater than was calculated. Besides this, the values of $P(F^* < 1)$ calculated according to formula (XI), as already has been observed, are underestimated; in reality they are greater. As for condition (II), it allows one to develop a simple formula for F^* , but the non-fulfillment of this condition would not be strongly reflected in the values of $P(F^* < 1)$. Since cases are possible where $\alpha_{ij} > \alpha_{i0} \cdot \alpha_{0j}$ and $\alpha_{ij} < \alpha_{i0} \cdot \alpha_{0j}$, then on the graph of $P(F^* < 1) = f(m)$ we could obtain a band of values of $P(F^* < 1)$, distributed on both sides of the curve $P(F^* < 1) = f(m)$, calculated for the assumption (II).

The calculation carried out above proved the high probability of the self-inhibition of chain reactions with sequential conversion of the products. We will examine the other extreme case, when all of the intermediate products are formed in parallel. Let us designate the fraction of the molecules RH which are converted into P_i by γ_i . Obviously,

$$F^* = \frac{1 + \sum \alpha_{0i} \pi_{ip}}{1 + \sum \alpha_i \alpha_{0i} \pi_{ip}} = \frac{2}{1 + \sum_{i=1}^m a_i \gamma_i} \quad (\text{XII})$$

For simplicity of the calculation, we will take all $\gamma_i = 1/m$, $a_i = 10^{x_i}$, x_i lying on the interval $[-b, b]$, with any of its values in this interval equally probable: then

$$F^* = \frac{2}{1 + \frac{1}{m} \sum 10^{x_i}}; P(F^* < 1) > 1 - \left(\frac{b + \lg m}{2b} \right)^m$$

The last formula is identical with formula (XI). Thus, even in the case of parallel formation of the intermediate products, the conclusion that the self-inhibition of complex chain reactions is highly probable remains in force. It is obvious that an analogous result will be obtained if reactions with sequential - parallel conversion of the products were included in the consideration. Exactly the same result is obtained by consideration of chain reactions in multi-component systems, for example, the oxidation of mixtures of hydrocarbons. The rate of such reactions in the overwhelming majority of cases must be smaller than the sum of the rates of conversion of the pure components for similar $[R_iH]$ and w_i because of the greater complexity of the composition of the radicals. The calculations carried out above convincingly show that increased complexity of the composition of the radicals during the reaction must with a high degree of probability lead to self-inhibition of complex chain reactions. These calculations explain cases of the self-inhibition of oxidation reactions and of cracking which are often met experimentally, and point to a change in the composition of the radicals as the fundamental cause of this phenomenon. The high probability of the self-inhibition of complex chain reactions is dependent on the fact that radicals with $a_i > 1$ more strongly inhibit the reaction than radicals with $a_i < 1$ accelerate it. In complex mixtures of radicals one can always expect the presence of both kinds of radicals, but radicals with $a_i > 1$ in the majority of cases overcome the action of radicals with $a_i < 1$, and the reaction is inhibited. In addition to the direct influence on the rate of chain reactions, the composition of the radicals can show an oblique influence - through the concentration of the intermediate product which guarantees a degenerate branching of the chain. This question has been considered [10], and it has been shown that a decrease of F usually leads to a decrease of the kinetic equilibrium concentration. Of the intermediate product and to an additional decrease of the rate of the reaction. The influence of the composition of the radicals on the concentration of the intermediate product increases the probability of the self-inhibition of degenerately branching chain reactions in comparison with non-branching chain reactions.

SUMMARY

The question of the probability of the self-inhibition of complex chain reactions was considered, and it was shown that a change in the composition of the radicals must lead with a high degree of probability to the self-inhibition of the complex chain reactions.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

MONO- π -CYCLOPENTADIENYL DERIVATIVES OF TITANIUM

A. N. Nesmeyanov, O. V. Nogina, and A. M. Berlin

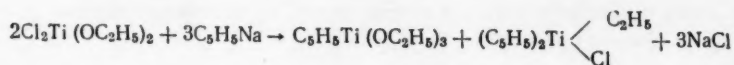
Institute of Heteroorganic Compounds, USSR Academy of Sciences

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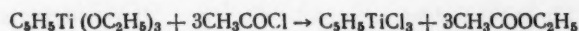
The chemistry of bis- π -cyclopentadienyl derivatives of titanium has been studied comparatively little, but on the basis of the published properties of $(C_5H_5)_2Ti$ [1-3] and comparison of the IR-spectra of $(C_5H_5)_2TiBr_2$ [4,5] with the spectra of ferrocene it has been concluded that bis-cyclopentadienyl compounds of titanium have a structure similar to that of ferrocene. For the properties of bis-pentadienyl derivatives see the reviews [6,7]. Trihalogeno-cyclopentadienyl derivatives of titanium have also been described in the literature [8,9] - these are compounds containing only one π -linked cyclopentadiene ring. The structure a π -cyclopentadienyltitanium trichloride has been settled convincingly [8,9].

We have studied the reaction of cyclopentadienyl sodium with dichlorodiethoxytitanium



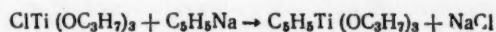
In this way we isolated a colorless mobile liquid, which distilled in vacuum, was very sensitive to moist air, and which corresponded to cyclopentadienyltriethoxytitanium by analysis and molecular weight. It is interesting to note that, in contradistinction to the normal alkoxy derivatives of titanium, this compound was not associated in solution and even at a concentration of 1.7 mol. % its molecular weight, determined by a cryoscopic method in benzene, corresponded to that calculated for the monomeric compound.

The structure of cyclopentadienyltriethoxytitanium as a π -cyclopentadienyl derivative of titanium was demonstrated by converting it with acetyl chloride into the cyclopentadienyltitanium trichloride discussed above [8,9].

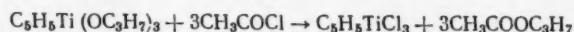


It should be noted that our cyclopentadienyltitaniumtrichloride, which we prepared more than once, melted 20° higher than the product described in the literature [8]. The second product from the reaction between dichlorodiethoxytitanium and cyclopentadienylsodium was a yellow crystalline substance which corresponded in analysis and molecular weight to bis-cyclopentadienylchloroethoxytitanium. The IR spectrum of this compound was very similar to that of bis-cyclopentadienylchlorotitanium.

In attempting to carry out the reaction between cyclopentadienylsodium and alkoxytitanium in such a way that the sole titanium containing product should be cyclopentadienyltrialkoxytitanium, we chose as the titanium starting material tri-n-propoxytitanium chloride. In fact the reaction went according to the scheme:

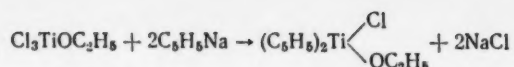


The cyclopentadienyl-tri-n-propoxytitanium obtained in this way (in 96% yield) resembled in its properties the cyclopentadienyltriethoxytitanium described by us above; in particular it was converted into cyclopentadienyltitanium trichloride by reaction with acetyl chloride:

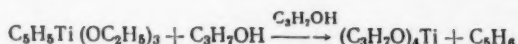


Next we took ethoxytitanium trichloride for reaction with cyclopentadienyl sodium. The reaction went

according to the equation

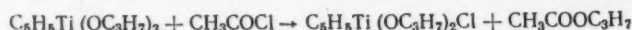


When an attempt was made to transesterify cyclopentadienyltriethoxytitanium with propanol it appeared that in mild conditions the alcohol decomposed the π -cyclopentadienyl compound with the formation of tetrakis-*n*-propoxytitanium.



In complete analogy, tetra-ethoxytitanium (95% yield) and cyclopentadiene (as cyclopentadienylthallium, 97% yield) were isolated from the reaction between cyclopentadienyltriethoxytitanium and ethanol.

Aiming to produce the mixed chlorides - alkoxides of cyclopentadienyltitanium, $\text{C}_5\text{H}_5\text{Ti}(\text{OR})\text{Cl}_2$ and $\text{C}_5\text{H}_5\text{Ti}(\text{OR})_2\text{Cl}$, we carried out the reaction of π -cyclopentadienyltripropoxytitanium with acetyl chloride in the ratios 1:2 and 1:1; the reactions went according to the schemes



The reaction products were golden-yellow viscous liquids which were decomposed by moist air, but which were stable on storage at lowered temperatures (1-5°).

EXPERIMENTAL

All the experiments described below were carried out with completely dry starting materials and under conditions which excluded traces of moisture.

Reaction of diethoxytitanium dichloride with cyclopentadienylsodium. A solution of cyclopentadienylsodium prepared from 4.5 g (0.194 M) sodium and 14.5 g (0.219 M) cyclopentadiene was cooled with ice and salt, and was added dropwise over half an hour to a vigorously stirred, ice and salt cooled solution of 20.2 g (0.097M) $(\text{C}_2\text{H}_5\text{O})_2\text{TiCl}_2$ in 30 ml tetrahydrofuran. The reaction mixture was stirred with cooling for a further 3 hr. The precipitate was filtered off and washed with tetrahydrofuran. The solvent was distilled from the filtrate in vacuum at 20-30 mm. Two products were separated from the residue: one of these was a colorless mobile liquid which distilled in vacuum b.p. 103° (2mm); 106-107° (3 mm); n_D^{20} 1.5500; yield 8.6 g (72% of theory). The substance was rapidly hydrolysed by moist air; it darkened on storage at room temperature, but it was stable on storage in a refrigerator. It was dissolved easily in all the usual organic solvents: C 52.87; 52.90; H 8.23; 8.13; Ti 19.18; 19.00% (cryoscopic method in benzene) 238. $\text{C}_5\text{H}_5\text{Ti}(\text{OC}_2\text{H}_5)_3$. Calculated: C 53.23; H 8.12; Ti 19.30% mol wt. 248.

The second reaction product was an orange crystalline substance which was recrystallized from a 1:1 mixture of benzene and petroleum ether; yield 4.3 g (34% of theory); m.p. 91-92°; easily soluble in chloroform, tetrahydrofuran, ethanol; less well in benzene and petroleum ether on storage at room temperature it darkened C 56.02; 55.74; H 5.77; 5.97; Ti 18.39; 18.69; Cl 13.47; 13.85% mol. wt (cryoscopic method in benzene) 250. $(\text{C}_5\text{H}_5)_2\text{TiCl}(\text{OC}_2\text{H}_5)$. Calculated: C 55.72; H 5.84; Ti 18.52; Cl 13.70% mol. wt. 258.

Reaction of tri-*n*-propoxytitanium chloride with cyclopentadienylsodium. The reaction was carried out in a similar way to the previous one. A solution of cyclopentadienylsodium, prepared from 1.8 g (0.079 M) sodium and 6.5 g (0.096 M) cyclopentadiene, was added to a solution of 20.4 g (0.079 M) $(\text{C}_3\text{H}_7\text{O})_3\text{TiCl}$ in 40 ml tetrahydrofuran. The reaction mixture was stirred while cooled in ice-salt mixture for 3 hr. The residue (21.9 g 96%), after filtration and removal of the solvent, was distilled in vacuum. A colorless liquid was obtained with b.p. 106-107° (0.5-1 mm); n_D^{20} 1.5310. It hydrolyzed rapidly in moist air. It darkened on storing at room temperature but was stable to storage in a refrigerator. It dissolved in all common organic solvents C 57.60; 57.69; H 9.17; 9.10; Ti 16.34; 16.03% mol. wt. (cryoscopic method in benzene) 282 $\text{C}_5\text{H}_5\text{Ti}(\text{OC}_3\text{H}_7)_3$. Calculated: C 57.92; H 9.02; Ti 16.50; mol. wt. 290.

Reaction of ethoxytitanium trichloride with cyclopentadienylsodium. The reaction was carried out in the same way as the first. A solution of cyclopentadienylsodium, prepared from 8.2 g (0.359 M) sodium and 25.8 g (0.389 M) cyclopentadiene, was added to a solution of 35.7 g (0.179 M) $C_2H_5OTiCl_3$ in 110 ml tetrahydrofuran. The reaction mixture was stirred for 3 hr while being cooled in an ice/salt mixture. A crystalline mass remained after filtration and evaporation of the solvent. From this 27.9 g (61%) of product was separated, m. p. 89-91° (from a mixture of benzene and petroleum ether) Found: C 55.38; 55.49; H 5.77; 5.66; Ti 18.45; 18.77% (C_5H_5)₂ TiCl (OC_2H_5). Calculated: C 55.72; H 5.84; Ti 18.52%. The chlorine content was determined on an aliquot Cl 13.42; 13.31%. Cl 13.70%; 4.9 g $C_5H_5Ti(OC_2H_5)_3$ was separated as a by-product 97-98° (1.5 mm); n_D^{20} 1.5498.

Reaction of $C_5H_5Ti(OC_2H_5)_3$ with acetylchloride at a reagent ratio of 1 : 3. To a solution of 2.76 g (0.011 M) $(C_2H_5O)_3TiC_5H_5$ in 20 ml petroleum ether was added a solution of 2.76 g (0.035 M) of freshly distilled acetyl chloride in 10 ml petroleum ether dropwise with stirring and cooling. The reaction mixture was stirred for a further half hour in the cold. On the following day the precipitate was filtered off, and the solvent and ethyl acetate removed from the filtrate. The yield of the moist product was quantitative. The substance was recrystallized from a mixture of methylene chloride and petroleum ether (1 : 4) or xylene: m. p. 207-208°. Literature data [9]: m.p. 145.5-147° (from xylene) and [8]: ~185° (from methylene chloride and pentane) Found: C 27.23; 27.23; H 2.24; 2.30; Ti 21.73; Cl 48.15; 48.35%. $C_5H_5TiCl_3$. Calculated: C 27.37; H 2.30; Ti 21.83; Cl 48.48%.

Reaction of $(C_3H_7O)_3TiC_5H_5$ with acetyl chloride at a reagent ratio of 1 : 3. The experiment was carried out in a similar way to the previous one. To 2 g (0.007 M) $(C_3H_7O)_3TiC_5H_5$ in 20 ml petroleum ether was added a solution of 2.2 g (0.028 M) acetyl chloride in 5 ml petroleum ether. The yield of product was quantitative: m.p. 207-208° (from xylene). Literature data [9] 145.5-147° in [8] m. p. 185°. Found: C 28.02, 27.95; H 2.34; 2.40; Ti 22.19; 21.85; Cl 47.53; 47.40%. $C_5H_5TiCl_3$. Calculated: C 27.37; H 2.30; Ti 21.83; Cl 48.48%.

Transesterification $C_5H_5Ti(OC_2H_5)_3$ with n-propanol. To 5 g (0.02 M) $C_5H_5Ti(OC_2H_5)_3$ was added 15 ml absolute propanol (3-fold excess) and the mixture was heated for one hour at a bath temperature of 70-80°. The alcohol and cyclopentadiene were distilled in vacuum at 20-30 mm. A further 10 ml propanol was added and distilled a second time. The residue was distilled in vacuum to give 5.52 g (96%) of a viscous, colorless liquid; b. p. 136° (1 mm); n_D^{20} 1.4976. Literature data [10]: b. p. 136-137° (1 mm); n_D^{20} 1.4979.

Effect of ethanol on $C_5H_5Ti(OC_2H_5)_3$. A solution of 3.5 g (0.014 M) $C_5H_5Ti(OC_2H_5)_3$ in 15 ml absolute ethanol was heated for 1 hr at a bath temperature of 80-90°. Then the mixture of ethanol and cyclopentadiene was slowly distilled at atmospheric pressure into a trap cooled with solid carbon dioxide. Into the reaction flask was placed a further 5 ml of ethanol, and a second distillation was carried out under the same conditions. The residue was distilled in vacuum to give 3.05 g (95%) of a viscous colorless liquid; b. p. 128-129° (2 mm); n_D^{20} 1.5096. Literature data [10]: b. p. 130-132° (2 mm); n_D^{20} 1.5099.

The strongly cooled mixture of alcohol and cyclopentadiene was added to cold thallium reagent [11] (5 g Tl_2SO_4 , 2 g KOH in 40 ml water). The yellowish precipitate was filtered off, washed with water, and dried. The weight of cyclopentadienylthallium was 3.74 g (98%); the product was twice sublimed in vacuum (2 mm) at a bath temperature of 110-115°. Found: C 22.29; 22.25; H 1.85; 1.84%. C_5H_5Tl . Calculated: C 22.29; H 1.87%.

Reaction of $C_5H_5Ti(OC_3H_7)_3$ with acetyl chloride at a reagent ratio of 1 : 1. To a solution of 2.08 g (0.0069 M) $C_5H_5Ti(OC_3H_7)_3$ in 15 ml petroleum ether (30-50°) was added in the cold a solution of 0.58 g (0.0069 M) acetyl chloride in 5 ml petroleum ether. On the following day the solvent and propyl acetate were distilled off C 49.77; 49.61; H 7.84; 7.65; Ti 17.50; 17.64% mol. wt. (cryoscopic method in benzene) 270. $C_5H_5TiCl(OC_3H_7)_2$. Calculated: C 49.55; H 7.18; Ti 17.96%; mol. wt. 267. The yield of undistilled product was quantitative. The substance decomposed on distilling in vacuum (1 mm). The product distilled over a wide temperature range - from 132-145°.

Reaction of $C_5H_5Ti(OC_3H_7)_3$ with acetyl chloride at a reagent ratio of 1 : 2. To a solution of 3.27 g (0.011 M) $C_5H_5Ti(OC_3H_7)_3$ in 20 ml petroleum ether was added in the cold a solution of 1.8 g (0.022 M) acetyl chloride in 5 ml petroleum ether. On the following day an oil had precipitated from the reaction mixture. The oil crystallized in solid carbon dioxide. The overall yield of the product was 2.65 g (96%). The substance was a golden yellow oil which distilled in vacuum at 159-161° (2 mm). It was easily hydrolyzed by moist air, but it was stable on storage in a refrigerator. Found: C 39.23; 39.36; H 4.99; 5.12; Ti 28.85; 29.57; 28.98; Cl 19.52; 19.14%; mol. wt. (cryoscopic method in benzene) 238. $C_5H_5TiCl_2(OC_3H_7)$. Calculated: C 39.54; H 4.97; Ti 29.18; Cl 19.71%; mol. wt. 243.

SUMMARY

1. By the reaction of cyclopentadienylsodium with $(C_2H_5O)_2 TiCl_2$ and $(C_3H_7O)_3 TiCl$, $C_5H_5Ti(OC_2H_5)_3$ and $C_5H_5Ti(OC_3H_7)_3$ were obtained. Some of their properties were studied.

2. Mixed chlorides-alkoxides of π -cyclopentadienyltitanium were prepared: $(C_5H_5)_2Ti(OC_2H_5)Cl$, $C_5H_5Ti(OC_3H_7)(Cl)_2$ and $C_5H_5Ti(OC_3H_7)_2Cl$.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

FLUORINE CONTAINING β -LACTONES

PART 2. β -TRIFLUOROMETHYL- β -METHYL- β -PROPIOLACTONE

I. L. Knunyants and Yu. A. Cheburkov

Institute of Hetero-organic Compounds, USSR, Academy of Sciences)

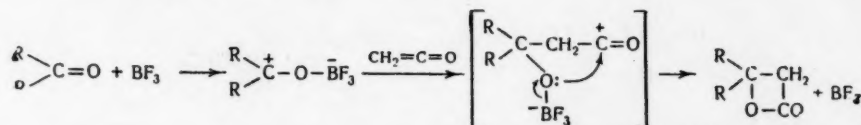
Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, 1961, No. 5, pp. 808-810, May, 1961

Original article received March 21, 1960

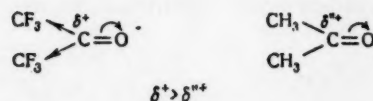
Corrected version received Feb. 4, 1961

In a previous paper [1] the preparations of β , β -bis-trifluoromethyl- β -propiolactone from hexafluoroacetone and ketene, and from the dehydration of β , β -bis-trifluoromethyl- β -hydroxypropionic acid, were reported. It appeared interesting to study the behaviour of β -trifluoromethyl- β -hydroxybutyric acid in this reaction and also to compare the reactivity of acetone, trifluoroacetone and hexafluoroacetone towards ketene.

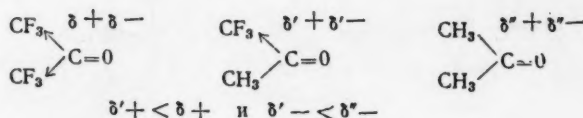
It is known that non-fluorinated ketones, in particular acetone, react with ketene only in the presence of acid catalysts, for example boron trifluoride etherate [2]. The reaction is begun by an electrophilic attack by the catalyst on the oxygen atom of the carbonyl group. The carbon atom in the bipolar ion thus formed is sufficiently electrophilic to react with the weakly nucleophilic ketene:



In hexafluoroacetone the carbon-oxygen double bond is sufficiently activated by the strong electron withdrawing effect of the trifluoromethyl group that it reacts with ketene without preliminary activation and a temperature of -80° .



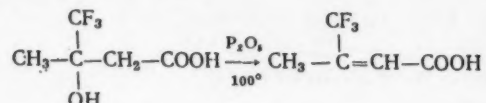
It appeared that 1,1,1-trifluoroacetone was more inert towards ketene than either hexafluoroacetone or acetone -the corresponding β -lactone is formed only in the presence of an acid catalyst and at a temperature not lower than -20° , whereas acetone reacts even at -60° . This is explained by the presence of a trifluoromethyl group which decreases the nucleophilicity of the carbonyl oxygen and therefore the reaction between the ketone and the electrophilic boron trifluoride molecules is made more difficult. On the other hand, the increased electrophilicity of the carbon atom caused by one trifluoromethyl group is insufficient to cause a direct reaction between trifluoroacetone and ketene



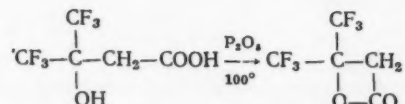
Thus, the stepwise substitution of fluorine atoms for the hydrogen atoms in the methyl groups of acetone leads to a qualitative change so that the ketone is converted from a nucleophilic agent (acetone and trifluoroacetone in

their reaction with ketene) to an electrophilic agent (hexafluoroacetone in the same reaction).

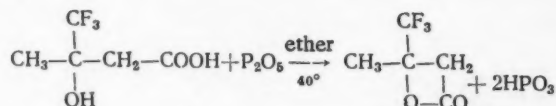
The structure of the lactone obtained was confirmed by synthesizing it from β -trifluoromethyl- β -hydroxybutyric acid. In 1955 Walborsky [3] found that β -trifluoromethylcrotonic acid was obtained on heating β -trifluoromethyl- β -hydroxybutyric acid with phosphorus pentoxide at 100°.



We have previously established that β , β -bis-trifluoromethyl- β -hydroxypropionic acid cyclizes to form a β -lactone under the same conditions.

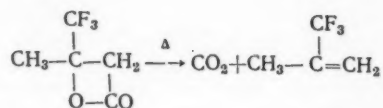


It appeared interesting to study in more detail the effect of dehydrating agents on β -trifluoromethyl- β -hydroxybutyric acid to try to cyclize it to the β -lactone. On dehydrating β -trifluoromethyl- β -hydroxybutyric acid with phosphorus pentoxide and distilling off the products (at a temperature of about 150-180°) we did not succeed in separating any individual substance. However under milder conditions (boiling with absolute ether) β -trifluoromethyl- β -methyl- β -propiolactone was obtained in good yield:

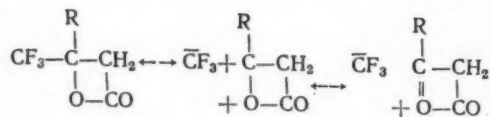


Study of the properties of the lactone obtained showed that it polymerized easily in the presence of mineral acids. Evidently as a result of this it was not possible to obtain the lactone by distillation from a mixture of phosphorus pentoxide and the metaphosphonic acid formed during the reaction.

β -Trifluoromethyl- β -methyl- β -propiolactone undergoes reactions characteristic of β -lactones; thus, for example, on heating it decomposes into carbon dioxide and trifluoroisobutene (II):



The thermal decomposition of this lactone began at 290° in distinction from β , β -dimethyl- β -propiolactone which begins to decompose at 60-70°. The bond between the tertiary carbon atom and the oxygen atom (which is ruptured on pyrolysis) is stronger in β -lactones having a trifluoromethyl group in the β -position:



This explains the increased thermal stability of fluorine-containing lactones.

EXPERIMENTAL

β -Trifluoromethyl- β -methyl- β -propiolactone (I). A solution of 104 g (0.93 M) trifluoroacetone in 200 ml absolute ether was placed in a four-necked flask equipped with a stirrer, a dropping funnel, a gas inlet tube, and a condenser cooled with dry ice/acetone. Ketene (75 g, 1.80 M) was bubbled under the stirred and ice-cooled ether during 5 hr, and 4.45 g boron trifluoride etherate in 50 ml absolute ether was added dropwise at the same time. On another day the catalyst was neutralized by adding 5.9 g dicyclohexylamine. The ether was evaporated off and the residue distilled in vacuum. The crude product obtained (103.8 g, 72%) boiled at 41-48° (10 mm). A second distillation gave the pure substance; m. p. 93-94° (155 mm); 140° (750 mm); m.p. 11-7°; n_D^{20} 1.3560; d_4^{20} 1.297; Found: MR 25.92; calculated: MR 25.62. Found: C 39.40; H 3.45; F 37.77%. $C_5F_3H_5O_2$. Calculated: C 38.98; H 3.25; F 37.00%.

In a flask with a reflux condenser a mixture of 9.89 g (0.057 M) β -trifluoromethyl- β -hydroxybutyric acid, 8.92 g (0.060 M) phosphorus pentoxide, and 200 ml absolute ether were refluxed for 5 hr. On another day the liquid was decanted from the solid, the ether evaporated off, and the residue distilled in vacuum. 3.22 g of a liquid with b. p. 34-35° (8 mm); n_D^{20} 1.3534 was collected. The residue in the flask crystallized. It was recrystallized from n-pentane to give 4.17 g of the initial hydroxyacid; m.p. 37.5-39.0°. The liquid obtained was the β -lactone (I); m.p. -4.5° to -4°. A mixture of this with the product from the previous experiment melted from -10° to -4°. The yield was 63a based on the hydroxyacid consumed in the reaction. With aniline the lactone gave the anilide of β -trifluoromethyl- β -hydroxybutyric acid* which was identical with that obtained from aniline and the product from the previous experiment. The lactone polymerized easily on heating with sulphuric acid, boron trifluoride etherate, or phosphorus pentoxide, giving a liquid polymer.

3,3,3-Trifluoroisobutene (II) Pyrolysis of the lactone (I) was carried out in the apparatus described in a preceding paper [1]. The lactone began to decompose when the temperature of the spiral was 290°. Pyrolysis occurred easily at 340-360°. From 8.9 g lactone was obtained 5.89 g of a liquid which, on distillation, gave 5.23 g (82%) of trifluoroisobutene, b.p. 4.9-5.3°; literature data: b.p. 6.4°. Found: C 41.16; H 4.26; F 54.37%; mol. wt. 110.3, $C_4F_3H_5$. Calculated: C 43.53; H 4.54; F 51.80%; mol. wt. 110.0.

SUMMARY

1. Trifluoroacetone reacts with ketene with the formation of β -trifluoromethyl- β -methyl- β -propiolactone.
2. This lactone is also obtained by dehydrating β -trifluoromethyl- β -hydroxybutyric acid with phosphorus pentoxide.
3. β -Trifluoromethyl- β -methyl- β -propiolactone decomposes thermally to give 3,3,3-trifluoroisobutene.

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* See following paper.

FLUORINE CONTAINING β -LACTONES

PART 3. OPENING OF THE FOUR MEMBERED RING IN β -TRIFLUOROMETHYL- β -METHYL- β -PROPIOLACTONE

I. L. Knunyants and Yu. A. Cheburkov

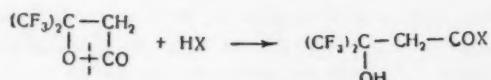
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Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, 1961, No. 5,

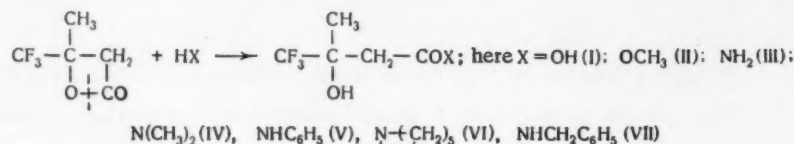
pp. 811-813, May, 1961

Original article received March 21, 1960

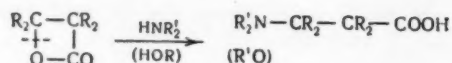
In the first paper of this series [1] the preparation of β, β -bis-trifluoromethyl- β -propiolactone was described. The most characteristic property of this lactone, which distinguished it from other β -lactones, was the unidirectional opening of the ring at the bond between the oxygen atom and the carbonyl group:



It was interesting to discover whether this unidirectional ring opening was retained on replacing one of the trifluoromethyl groups by a methyl and also to find out to what extent the rupture of the bond between the tertiary carbon atom and the oxygen atom proceeds. This reaction is known for β -lactones not containing fluorine, in particular β, β -dimethyl- β -propiolactone [2]. It was shown that β -trifluoromethyl- β -methyl- β -propiolactone reacted easily with water, methanol, ammonia and various amines, and it was converted in this way to β -trifluoro-methyl- β -hydroxybutyric acid and its derivatives:



The reactions between β -trifluoromethyl- β -methyl- β -propiolactone and amines or alcohol were carried out under conditions in which ordinary β -lactones give β -amino or β -alkoxy-acids as the result of ring fission at the bond between the ester oxygen atom and the carbon atom [3]



However we did not discover a parallel reaction in the fluorolactone investigated.

Thus, the presence of a single trifluoromethyl group in the β -position is sufficient to make the ring-opening of the four membered β -lactone ring completely unidirectional at the bond between the oxygen atom and the carbonyl group.

EXPERIMENTAL

β -Trifluoromethyl- β -hydroxybutyric acid. A mixture of 0.86 g lactone and 3 ml 50% sulphuric acid were shaken until the lactone dissolved completely; it was then decomposed with water and extracted with ether. After drying the solution, the ether was evaporated, and the residue was recrystallized from *n*-heptane to give 0.85 g (88%) of the hydroxyacid (I) with m. p. 43-43.5°. Literature data [4]: m. p. 30°, b. p. 75-76° (2 mm). Found: C 34.87; H 4.14; F 33.41%. $\text{C}_5\text{F}_3\text{H}_7\text{O}_3$. Calculated: C 34.90; H 4.07; F 33.14%.

The reaction between the lactone and concentrated hydrochloric acid required the mixture to be heated for some hours, for its accomplishment; the yield was quantitative.

Methyl β -trifluoromethyl- β -hydroxybutyric acid. 16.6 g lactone was added with cooling to a solution of sodium methoxide in methanol, obtained from 1.1 g sodium and 100 ml methanol. The mixture was then heated under reflux for 10 hr. After removing the excess methanol the residue was cooled and acidified with concentrated hydrochloric acid. An oil precipitated and was separated by extracting with ether. After drying and evaporation of the solvent 15.0 g (75%) of a colorless liquid was obtained. It dissolved in the cold in 20% alkali; it reacted with metallic sodium in ether solution: b. p. 164-165° (753 mm); n_D^{20} 1.3754; d_4^{20} 1.290; Found MR 33.04; Calculated MR 33.51. Found: C 38.77; H 4.98; F 30.40%. $C_6F_3H_5O_3$. Calculated: C 38.71; H 4.83; F 30.65%.

When the hydroxyacid (I) was esterified with methanol in the presence of sulphuric acid the ester (II) was obtained in 75% yield.

14.0 g (0.091 M) lactone was added with cooling to a solution of 6.8 g (0.21 M) absolute methanol in 24 g anhydrous sulphuric acid. The mixture was then heated at 100° for 7 hr. after which it was decomposed with water. The precipitated oil was separated by extraction with ether. After drying the mixture and evaporating the solution 12.05 g of a product was obtained. After rectification through a 200 mm column it gave 9.3 g (55%) of the hydroxy-ester (II) with b.p. 163-164° (754 mm); n_D^{20} 1.3754 and 1.5 g of a fraction with b. p. 114-116° (754 mm); n_D^{20} 1.3713 which was methyl β -trifluoromethylcrotonic acid. Yield 10%. Literature data [5]: b. p. 112.5-113.5° (753 mm); n_D^{20} 1.3718.

β -Trifluoromethyl- β -hydroxybutyramide. 1.05 g β -lactone was dissolved in 5 ml concentrated liquid ammonia. After evaporating to dryness and recrystallizing from 100 ml carbon tetrachloride 1.09 g (93%) of crystals with m.p. 78° was obtained. C 34.88; H 4.83; F 32.23; N 8.24%. $C_5F_3H_5O_2N$. Calculated: C 34.90; H 4.66; F 33.14; N 8.14%.

On treating the ester (II) with aqueous ammonia the amide (III) was obtained only in 46% yield; most of the ester was hydrolyzed into the hydroxyacid (I).

The Dimethylamide of β -trifluoromethyl- β -hydroxybutyric acid. 0.6 g Dimethylamine was passed into a solution of 1 g of the lactone in 5 ml acetonitrile for 1 hr. At the end of the reaction the acetonitrile and the excess dimethylamine was evaporated and the residue recrystallized over 24 hr. 1.26 g (98%) of crystals (m.p. 36.5° from hexane) were obtained. The amide (IV) dissolved in water and organic solvents. C 42.27; H 6.10; F 30.27; N 7.00%. $C_7F_3H_{12}O_2N$. Calculated: C 42.21; H 6.04; F 28.65; N 7.04%.

Anilide of β -trifluoromethyl- β -hydroxybutyric acid. The anilide was obtained in 87% on mixing equimolecular quantities of the lactone and aniline, m.p. 93° (from carbon tetrachloride). Found: C 53.17; H 4.93; F 23.53; N 5.63%. $C_{11}F_3H_{12}O_2N$. Calculated: C 53.46; H 4.85; F 23.08; N 5.67%. The amides (V)-(VII) did not dissolve in water and dilute hydrochloric acid.

Piperidide of β -trifluoromethyl- β -hydroxybutyric acid. The piperidide was obtained in 77% yield, m. p. 35-36° (from hexane) Found: C 50.27; H 6.68 F 24.40; N 5.90%. $C_{10}F_3H_{16}O_2N$. Calculated: C 50.20; H 6.68; F 23.85; N 5.85%.

Benzylamide of β -trifluoromethyl- β -hydroxybutyric acid. Benzylamine, 0.66 g (0.0062 M), was added dropwise to a solution of the lactone, 0.95 g (0.006 M) in 3 ml acetonitrile. The residue which initially precipitated redissolved during further addition of the benzylamine. After evaporation of the acetonitrile 1.62 g (quantitative yield) of crystals with m. p. 76.2° (from carbon tetrachloride) was obtained C 54.94; H 5.43; F 21.62; N 5.54%. $C_{12}F_3H_{14}O_2N$. Calculated: C 55.19; H 5.36; F 21.84; N 5.37%.

SUMMARY

Ring opening of β -trifluoromethyl- β -methyl- β -propiolactone is unidirectional and leads to derivatives of β -trifluoromethyl- β -hydroxybutyric acid.

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FLUORINE CONTAINING β -SULTONES

PART 7. USE OF TETRAFLUOROETHANE- β -SULTONE IN ACETYLATION

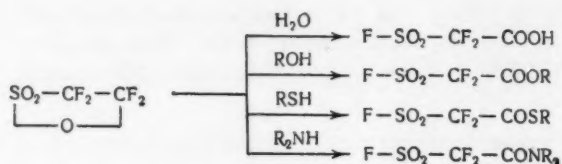
G. A. Sokol'skii and I. L. Knunyants

Institute of Hetero-organic Compounds, USSR Academy of Sciences

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, 1961, No. 5, pp. 813-815, May, 1961

Original article received 18 April, 1960.

We reported earlier [1] that fluorine containing β -sultones reacted energetically with various compounds which contained active hydrogen atoms. The products of this reaction were shown to be the corresponding derivatives of fluorine substituted β -fluorosulfonyl-carboxylic acids, for example:

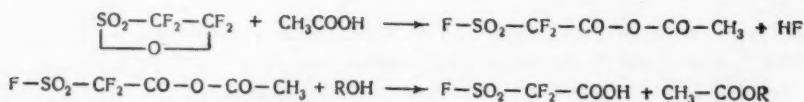


It might be expected that the interaction of fluorine containing β -sultones with carboxylic acids would occur in an analogous way; in this case the reaction products ought to be mixed anhydrides of the corresponding carboxylic and β -fluorosulfonyl-carboxylic acid. The properties of these compounds should undoubtedly be analogous to the properties of known mixed acid anhydrides which possess energetic acylating properties [2].

TABLE

No. of expts.	Alkyl acetate	Acyla- tion temp. °C	Separa- tion technique	Yield, %	No. of expts.	Alkyl acetate	Acyla- tion temp. °C	Separa- tion technique	Yield, %
1	Methyl acetate	0	A	98	10	β-Chloroethyl acetate	10	B	88
2	Ethyl acetate	0	A	98	11	β-Methoxyethyl acet.	10	B	85
3	n-Propyl acetate	0	A	98	12	Allyl acetate	10	B	80
4	i-Propyl acetate	0	A	95	13	Phenyl acetate	20	B	72
5	n-Butyl acetate	10	A	95	14	p-Tolyl acetate	20	B	70
6	n-Amyl acetate	10	B	92	15	Glycol monoacetate	10	B	75
7	n-Hexyl acetate	20	B	90	16	Glycerol monoacetate	10	B	70
8	cyclo-Hexyl acetate	20	B	80	17	Glycol diacetate	20	B	80
9	Benzyl acetate	20	B	85	18	Glycerol triacetate	20	B	77

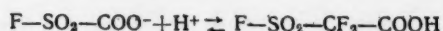
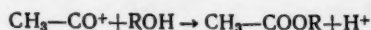
In fact on mixing tetrafluoroethane- β -sultone with glacial acetic acid (taken in equimolar quantities) an energetic reaction was observed, accompanied by spontaneous heating of the mixture and evolution of hydrogen fluoride. The formation of a mixed anhydride of fluorosulfonyl-difluoroacetic and acetic acids was confirmed by the formation of the corresponding alkyl acetates when the reaction mixture was treated with various alcohols (see the table). Fluorosulfonyl-difluoroacetic acid occurred with the other products of alcoholysis of the mixture of tetrafluoroethane- β -sultone and acetic acid. The process is described by the following equations:



Analogous results were obtained by using substituted and unsaturated alcohols, and also phenols.

The formation of the corresponding half or complete ester occurs in acylation of multiatomic alcohols, depending on the order of mixing the reagents and the quantity of multiatomic alcohols used. Thus, on adding an equimolar mixture of tetrafluoro- β -sultone and acetic acid to an equimolar quantity of glycol, glycol monoacetate is formed, whereas on adding a half molar quantity of glycol to a mixture of the sultone and acid, glycol diacetate is formed. In a similar way glycerol monoacetate and glycerol triacetate are obtained.

The absence of esters of fluorosulfonyldifluoroacetic acid from the reaction products and the exclusive production of alkyl acetates are in line with known ideas on the mechanism of acylation with mixed anhydrides. There is no doubt that the mixed anhydride formed under the conditions given is inclined to dissociate in one way only - into a fluorosulfonyldifluoroacetate anion and an acetyl cation; the latter acylates the alcohol or phenol.



This direction of dissociation of the mixed anhydride is explained by the considerable difference in strength of acetic and fluorosulfonyldifluoroacetic acids.

Thus, tetrafluoroethane- β -sultone can be successfully used as a reagent which considerably facilitates the esterification of alcohols and phenols with acetic acid. There is no doubt that esterification with other carboxylic acids could be carried out in a similar way. It is evident that other fluorine containing β -sultones could be used for this purpose.

EXPERIMENTAL

Acetylation of alcohols. Glacial acetic acid (0.1 m) was added to stirred and ice cooled tetrafluoroethane- β -sultone (0.1 M) in a teflon reactor. At a temperature of 0-20° (see Table) the absolute alcohol (0.1 M) was added. The reaction mixture was poured into a cooled solution of potassium fluoride (10 g) in water (30 ml). The alkyl acetate was isolated by one of the methods A or B: A. The only layer was separated, dried over magnesium sulfate, and distilled. B. The mixture was extracted with ether; the ether extracts were combined, dried over magnesium sulfate, and fractionated.

Glycol diacetate was obtained in an analogous manner from 0.1 M tetrafluoroethane- β -sultone, 0.1 M acetic acid, and 0.05 M glycol.

Glycerol triacetate was obtained similarly from 0.1 M tetrafluoroethane- β -sultone, 0.1 M acetic acid, and 0.033 M glycerol.

Glycol monoacetate. A mixture of 0.1 M tetrafluoroethane- β -sultone and 0.1 M acetic acid was added dropwise with stirring at room temperature to 0.1 M glycol. The product was worked up by method B.

Glycerol monoacetate was obtained similarly from 0.1 M glycerol and a mixture of 0.1 M tetrafluoroethane- β -sultone and 0.1 M acetic acid.

Isolation of fluorosulfonyldifluoroacetic acid. To an equimolar mixture of tetrafluoroethane- β -sultone and glacial acetic acid an equal quantity by weight of ethanol was added with stirring and cooling. The solution was twice dehydrofluorinated with calcined potassium fluoride. It was then fractionated by heating on the water bath initially at atmospheric pressure and then at reduced pressure. Fluorosulfonyldifluoroacetic acid [3] was isolated by a second distillation at atmospheric pressure. The yield was 95%. In a similar way a 92% yield of fluorosulfonyldifluoroacetic acid was obtained when methanol was used.

SUMMARY

1. The reaction between tetrafluoroethane- β -sultone and glacial acetic acid has been studied.

2. A new method for preparing acetates has been developed. It consists of treating an alcohol or phenol with an equimolar mixture of tetrafluoroethane- β -sultone and acetic acid.

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3. M. A. Dimitriev, G. A. Sokol'skii, and I. L. Knunyants, Izv. AN SSSR. Otd. Khim. Nauk (1960) p. 1035.

All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

IMIDES OF ACIDS OF PHOSPHORUS

COMMUNICATION 5. THE REACTION OF TRIALKYL PHOSPHITES WITH HYDRAZOIC ACID

M. I. Kabachnik and V. A. Gilyarov

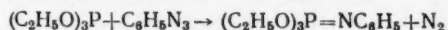
Institute of Heteroorganic Compounds, Academy of Sciences, USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otdelenie Khimicheskikh Nauk*, 1961, No. 5,

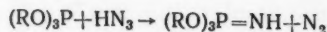
pp. 816-818, May, 1961

Original article submitted April 1, 1960

We have previously shown that trialkyl phosphites and esters of alkyl or aryl phosphinous acids can react with phenyl azide [1] and methyl azide [2] with liberation of nitrogen and formation of imidophosphates, for example



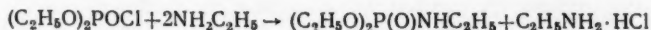
It was of interest to obtain the parental substances of the imidophosphate class, namely $(\text{RO})_3\text{P}=\text{NH}$. It could be assumed that substances of this type are formed by the reaction of trialkyl phosphites with hydrazoic acid, as follows



According to Staudinger and Hauser [3], with hydrazoic acid triphenyl phosphine and triethyl phosphine form triphenyl phosphineimine and triethyl phosphineimine respectively; these were isolated in the form of their salts with hydrazoic acid, for example $(\text{C}_6\text{H}_5)_3\text{P}=\text{NH} \cdot \text{HN}_3$. Free triphenyl phosphineimine was recently described, but it was obtained by other methods [4,5].

We found that the reaction of hydrazoic acid with trialkyl phosphites is complex. Liberation of nitrogen is completed in 2-3 days at room temperature, i. e., the reaction takes place far more slowly than with alkyl or aryl azides. The only reaction product which can be isolated from the products obtained when trimethyl phosphite reacts with hydrazoic acid is dimethyl-N-methylaminophosphate $(\text{CH}_3\text{O})_2\text{P}(\text{O})\text{NHCH}_3$. The following were isolated from the reaction products obtained from triethyl phosphite and HN_3 : diethyl-N-ethyl aminophosphate $(\text{C}_2\text{H}_5\text{O})_2\text{P}(\text{O})\text{NHC}_2\text{H}_5$, diethyl phosphite $(\text{C}_2\text{H}_5\text{O})_2\text{PHO}$ and diethyl aminophosphate $(\text{C}_2\text{H}_5\text{O})_2\text{PONH}_2$.

We proved the structure of diethyl-N-ethyl aminophosphate by cross synthesis from diethyl chlorophosphate and ethylamine



The constants of samples of the substance obtained by different methods agreed. In the Table: a) was obtained by reaction with hydrazoic acid; b) was obtained from diethyl chlorophosphate.

The structure of diethyl-N-ethyl aminophosphate is also confirmed by data of the infrared spectrum (the presence of $\text{P}=\text{O}$ and $\text{N}-\text{H}$ frequencies: 1240 and 3400 cm^{-1}) (Fig. 1).

In this reaction, diethyl aminophosphate is obtained in the form of a crystalline substance with an m.p. of 53.5-54.5°, which corresponds to literature data [6]. The substance does not give a depression of the melting point in a mixed sample with diethyl aminophosphate of known structure.

The presence of diethyl phosphite was proved by the constants of the liquid substance. When the reaction products of triisopropyl phosphite and hydrazoic acid were distilled, we obtained a fraction with a b.p. of 86-89° (2 mm), containing, according to analytical data, diisopropyl-N-isopropyl aminophosphate (contaminated with

TABLE

Serial No.	Formula	Yield, %	B.p., °C (p mm Hg).	n_D^{20}	d_4^{20}
1	$(CH_3O)_2P(=O)NHCH_3$	37,3	81 (1)	1,4260	1,2002
2	$(C_2H_5O)_2P(=O)NHC_2H_5$	a) 34,0 b) 56,4	92-94 (1) 96-97 (1)	1,4250 1,4258	1,0590 1,0590

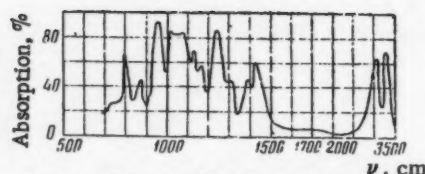
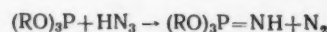


Fig. 1. Infrared absorption spectra of diethyl-N-ethyl aminophosphate (2a)

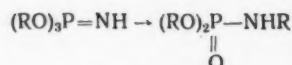
diisopropyl aminophosphate) and diisopropyl aminophosphate with an m.p. of 57°.

Therefore, when trialkyl phosphites react with hydrazoic acid, substances which may be considered as products of the further conversion of trialkyl imidophosphates or of secondary reactions are obtained instead of the expected trialkyl imidophosphates $(RO)_3P=NH$. The most probable of these reactions are as follows:

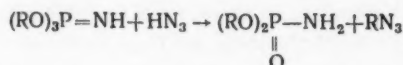
1) The initial reaction:



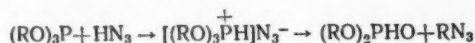
2) The Pischchimuki rearrangement of trialkyl imidophosphate.



3) The action of hydrazoic acid on trialkyl imidophosphate



4) The behavior of hydrazoic acid as an acid on trialkyl phosphite



EXPERIMENTAL

A benzene solution of hydrazoic acid (equimolar amount) was added dropwise with cold water cooling to trialkyl phosphite. The course of the reaction was controlled by the consumption of acid.

Reaction of trimethyl phosphite with hydrazoic acid. When 61.5 ml of a benzene solution containing 3.4 g of hydrazoic acid was added to 9.9 g of trimethyl phosphite, slow liberation of nitrogen was observed for a day. The solution was then alkaline to phenolphthalein. The benzene was distilled under vacuum; after two distillations of the residue we obtained 5.2 g of dimethyl-N-methyl aminophosphate. Found: C 26.21, 26.07; H 7.26, 7.22; P 22.36, 22.36; N 9.78, 9.99%. $C_3H_{10}O_3NP$. Calculated: C 25.90; H 7.24; P 22.27; N 10.01%.

The amide obtained was a readily mobile colorless liquid, soluble in water, alcohol, ether and petroleum ether.

Reaction of triethyl phosphite with hydrazoic acid. The reaction of 70 ml of a benzene solution containing 2.5 g of hydrazoic acid and 9.5 g of triethyl phosphite was completed in 2 days. After two distillations we obtained

three fractions: I) 1.1 g, b. p. 40-41° (1 mm); n_D^{20} 1.4175; this consisted mainly of diethyl phosphite; II) 3.5 g (for constants, see Table), consisting of diethyl-N-ethyl aminophosphate. Found: C 39.58; 39.51; H 8.80; 8.91; P 17.20; 17.07; N 7.39; 7.48%, $C_6H_{16}O_3NP$. Calculated: C 39.77; H 8.90; P 17.10; N 7.72%. III) 0.9 g, b. p. 106° (0.1 mm); the substance crystallized the m. p. was 48.50°; after recrystallization from petroleum ether with a small amount of benzene the m. p. was 53.5-54.5°. Found: N 9.26; 9.46%, $C_4H_{12}O_3NP$. Calculated: N 9.15%.

The melting point of a mixed sample with known diethyl aminophosphate was 53.5-54.5°. Literature data for diethyl aminophosphate are [6] b. p. 137-138° (0.1 mm); m. p. 54.5°.

Diethyl-N-ethyl aminophosphate. A. quantity of 15.2 g diethylchlorophosphate was added dropwise with stirring and cooling to a solution of 8.0 g of ethylamine in 80 ml of absolute ether. The mixture was then stirred for 1 hour with cooling and for 2 hours at room temperature. The precipitate was separated, washed on a filter with ether and the ethereal solution was dried with sodium sulfate. We obtained 9.0 g of diethyl-N-ethyl aminophosphate. Found: C 39.75; 39.90; H 8.78; 8.83; P 17.44; 17.22%. Literature data for diethyl-N-ethyl aminophosphate are [7]: b. p. 135° (25 mm).

The reaction of triisopropyl phosphite with hydrazoic acid. The reaction between 9.2 g of triisopropyl phosphite and 1.9 g of hydrazoic acid was completed in 2 days. After two distillations under vacuum we obtained 2.1 g of a liquid with a b. p. of 86-89° (1 mm); n_D^{20} 1.4220; d_4^{20} 0.9902. Found: C 47.50; 47.41; H 9.62; 9.45; P 13.74; 13.84%, $C_9H_{22}O_3NP$. Calculated: C 48.41; H 10.16; P 13.88%.

We also obtained 1.3 g of a substance with a b. p. of 106° (1 mm); the m. p. was 40-42°. After recrystallization from petroleum ether (b. p. 30-60°) the crystals melted at 57°. The yield of diisopropyl aminophosphate was 0.9 g (11%). Found: C 39.90; 39.65; H 8.72; 8.72; P 17.04; 17.27%, $C_6H_{16}O_3NP$. Calculated: C 39.75; H 8.90; P 17.10%.

SUMMARY

The principal products of the reaction of trialkyl phosphites with hydrazoic acid are dialkyl-N-alkyl aminophosphates; these are evidently formed by isomerization of the imidophosphates $(RO)_3P=NH$ initially obtained.

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IMIDES OF ACIDS OF PHOSPHORUS

COMMUNICATION 6. TRIALKYL-N-ACYL IMIDOPHOSPHATES

M. I. Kabachnik and V. A. Gilyarov

Institute of Heteroorganic Compounds, Academy of Sciences, USSR

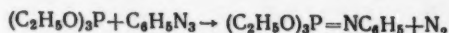
Translated from *Izvestiya Akademii Nauk SSSR*,

Otdelenie Khimicheskikh Nauk, 1961, No. 5,

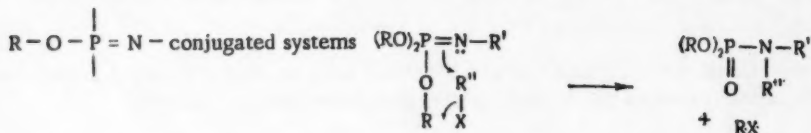
pp. 819-823, May, 1961

Original article submitted April 6, 1960

In previous investigations we obtained imidophosphates $(RO)_3P=NR'$ and imidophosphinates $R(R'O)2P=NR''$ by the reaction of trialkyl phosphites or dialkylalkyl phosphinites respectively with phenyl azide or methyl azide [1,2], for example

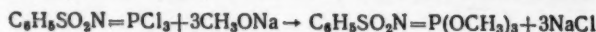


We investigated some reactions of trialkyl-N-phenyl imidophosphates: hydrolysis, acidolysis, alkylation, acylation, the reaction with carbon bisulfide. With the exception of the latter, the general type of these reactions consists in electrophilic attack at the unshared electron pair of the nitrogen atom, with subsequent (or simultaneous) removal of an alkyl radical of phosphoric ester and the appearance of a semipolar $P=O$ bond, i.e. type 1-4 reactions of $\sigma\pi$ -

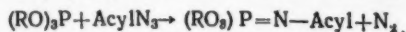


(hydrolysis: $R'' = H$, $X = OH$, acidolysis: $R'' = H$, $X = Cl$ or $X = C_6H_5COO$, alkylation: $R'' = Alk$, $X = I$, acylation: $R'' = Acyl$, $X = Cl$). Only the reaction with carbon bisulfide takes place like a 1-2 reaction.

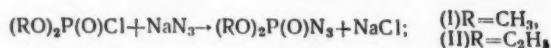
If these ideas are correct, a reduction in the nucleophilic character of the nitrogen atom of the imidophosphate must prevent these reactions. For this reason it was of interest to investigate the reaction of acyl imidophosphates of the type $(RO)_3P=N-Acyl$ and trace the variation of the reactivity of the $P=N$ group as a result of the introduction of electrophilic acyl substituents at the nitrogen atom. Substances of this type were obtained by Kirsanov and his co-workers by the reaction of N-acyl imido phosphorus chloride with sodium alcoholates, for example:



We obtained N-acyl imidophosphates by a new method, i.e. by reacting trialkyl phosphites with the azides of acids, for example with the azides of dialkyl phosphoric acids or methane sulfonic acid



There are few data on azides of phosphorus acids in the literature. Some patents give brief information on dialkyl azidothiophosphates $(RO)_2P(S'N)_3$ [4] and tetraalkyl diaminoazidophosphates $(R_2N)_2P(O)N_3$ [5], which have been proposed as insecticides. Only the boiling points of dialkyl azidothiophosphates were given, while tetraalkyl diaminoazido-phosphates were not isolated in the pure form. Azides of dialkyl phosphoric acids and methane sulfonic acid have not been described. It was found that to obtain dimethyl azidophosphate (I) and diethyl azidophosphate (II) * we could employ the method used by Schrader [4] for preparing azides of diethyl thiophosphoric acid: boiling (20 minutes) diethylchlorophosphate with excess sodium azide in acetone solution

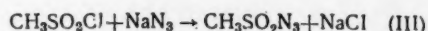


* Here and throughout the rest of the article the numbers of the substances, as listed in the Table, are given.

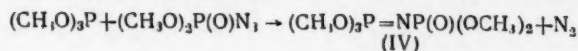
No. of the substance	Formula	Yield, %	B.p., °C (p. mm Hg).	n_D^{20}	d_4^{20}
I	$(CH_3O)_2P \begin{array}{c} \diagup O \\ \diagdown N_3 \end{array}$	34,8	79,5—81 (10)	1,4276	1,3013
II	$(C_2H_5O)_2P \begin{array}{c} \diagup O \\ \diagdown N_3 \end{array}$	45,0	69—70 (3)	1,4275	1,1718
III	$CH_3SO_2N_3$	74,4	59—60 (17)	1,4675	1,4361
IV	$(CH_3O)_3P=NP(O)(OCH_3)_2$	51,4	104—106 (0,2)	1,4430	1,3118
V	$(C_2H_5O)_3P=NP(O)(OC_2H_5)_2$	82,0	121 (0,5)	1,4345	1,1294
VI	$(C_2H_5O)_3P=NSO_2CH_3$	75,8	109—110 (0,2)	1,4500	1,2170
VII	$(C_2H_5O)_3P(O)NHP(O)(OC_2H_5)_2$	58,4	79—80 (0,001)	1,4415	1,2029
VIII	$(C_2H_5O)_3P(O)NHSO_2CH_3$	75,7	M.p. 96—96,5°		

However, the reaction of dimethyl chlorophosphate and diethyl chlorophosphate with an aqueous solution of sodium azide, with stirring for 1 hour and cooling, was found to be a more convenient method. This method was given among others in the patent [5] for obtaining tetraalkyl diaminoazidophosphates. The yields and constants of both azides are given in the Table; they are colorless liquids with a pleasant odor.

We employed the exchange reaction of halogen by an azide group, with treatment by an aqueous solution of sodium azide, for methyl sulfonyl chloride, obtaining in this way methane sulfazide (III)

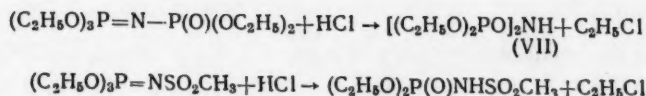


The azide of dimethyl phosphoric acid reacts smoothly with trimethyl phosphite, with formation of trimethyl-N-dimethyl phosphoryl imidophosphate (IV), as follows



The imidophosphates (V) and (VI) (see Table) were obtained in a similar way from azides of diethyl phosphoric acid and methane sulfonic acid. Figs. 1 and 2 give the infrared spectra of imidophosphates * (IV-VI). Attention is drawn to absorptions with maxima of 1338 cm^{-1} in the case of imidophosphate (IV) and 1324 and 1374 cm^{-1} for imidophosphate (V), which may be due to the presence of a $P=N$ group [2]. In the spectrum of imidophosphate (VI), it would appear that the absorption in the $1300\text{--}1350\text{ cm}^{-1}$ region may also be due to the $P=N$ group; however, it is known from literature data [6] that it is also characteristic of the SO_2 group.

An investigation of the properties of N-acyl imidophosphates (V) and (VI) showed the expected marked difference from those of N-alkyl or N-aryl imidophosphates: N-acyl imidophosphates do not react with carbon bisulfide when boiled for 5-6 hours, and they do not undergo change when heated in sealed tubes for 5 hours with ethyl iodide at $160\text{--}170^\circ$. Triethyl-N-diethyl phosphorylimidophosphate (V) is not hydrolyzed when boiled with water for 4 hours or when heated at $60\text{--}70^\circ$ with formic or acetic acid (2 hours); it was also resistant to the action of chlorine at room temperature for 20 min. However, dry hydrogen chloride reacts with imidophosphates, as follows



* The infrared spectra of imidophosphates (IV) and (V) were determined by E. M. Popov. The infrared spectrum of imidophosphate (VI) was determined in the optical laboratory of INEOS, Academy of Sciences, USSR, directed by I. V. Obreimov.

The aminophosphate (VII) obtained is titrated with aqueous alkali like a monobasic acid (thymolphthalein as indicator). When determined cryoscopically in benzene, the molecular weight of this compound was double and did not vary with a change in concentration. Such dimerization was not observed in glacial acetic acid.

According to our data, the action of dry hydrogen chloride is the best method of converting imidophosphates $(RO)3P=NR'$ to amides $(RO)2P-HNR'$, where R' is an alkyl or acyl radical.

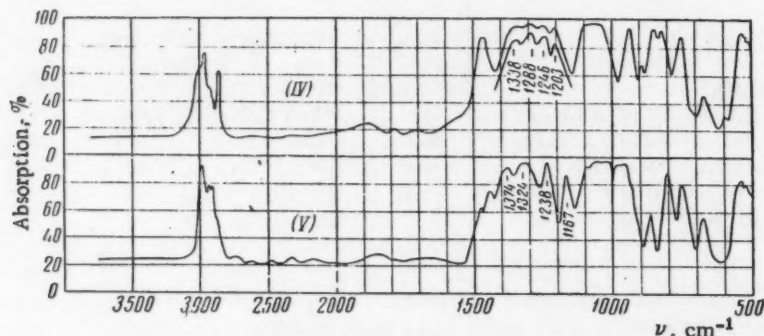


Fig. 1. Infrared spectra of imidophosphates (IV) and (V).

Therefore, the experimental data confirm the assumption of a reduction in the nucleophilic reactivity of imidophosphates as a result of the introduction of electrophilic substituents at the nitrogen of the imino group.

EXPERIMENTAL

A quantity of 34.5 g of diethyl chlorophosphate was added dropwise with stirring to 45.5 g of sodium azide under a layer of 200 ml of dry acetone; the mixture was boiled and stirred for 23 hours, the precipitate was separated, washed with ether, the solution was evaporated under vacuum and the residue was fractionated under vacuum. After four successive distillation we obtained 21.3 g (62.8%) of diethyl azidophosphate with a b.p. of 76-77° (4.5 mm); n_D^{20} 1.4260; d_4^{20} 1.1672; Found: C 26.4; 26.3; H 5.8; 5.0; P 16.9; 16.8%. $C_4H_{11}O_3N_3P$. Calculated: C 26.8; H 5.6; P 17.8; N 23.4%.

A quantity of 8.6 g of diethyl chlorophosphate was added dropwise with stirring to a solution of 11.6 g of sodium azide in 50 ml of water, with cooling by ice; the reaction mixture was then stirred for 1 hour at room temperature.

The product was extracted twice with chloroform (15 ml each time). The chloroform solution was dried over calcined sodium sulfate for 4 hours, the solution was driven off under vacuum and the residue was distilled. We obtained 4.9 g (45%) of diethyl azidophosphate with a b.p. of 69-70° (3mm); n_D^{20} 1.4275; d_4^{20} 1.1718. Found: C 27.2; 27.2; H 5.6; 5.7; P 16.8, 16.8; N 23.6; 23.8%. Diethyl azidophosphate is a colorless liquid with a pleasant odor, soluble in organic solvents and insoluble in water.*

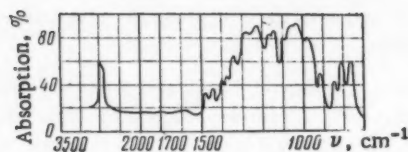


Fig. 2. Infrared spectra of imidophosphate (VI).

Dimethyl azidophosphate. This compound was obtained from 58.6 g of dimethyl chlorophosphate and 91 g of sodium azide in 400 ml of water. The yield was 21.9 g (34.8%); the b.p. was 79.5-81° (10 mm); n_D^{20} 1.4276; d_4^{20} 1.3013. Found: C 16.6, 16.4; H 4.0, 4.0; P 20.6, 20.6%. $C_2H_6O_3N_3P$. Calculated: C 15.9; H 4.0; P 20.6%.

Methane sulfazide. This was obtained from 11.5 g of methane sulfonyl chloride and 19.5 g of sodium azide in 50 ml of water. The yield was 9.0 g (74.4%); the b.p. was 59-60° (17 mm); n_D^{20} 1.4675; d_4^{20} 1.4361. Found: N 35.0, 35.1%. $CH_3O_2N_3S$. Calculated N 37.7%. Methane sulfazide is a colorless liquid, decomposing with an explosion at 125-130°.

* Dimethyl and diethyl azidophosphates have a considerable mitotic effect.

Trimethyl-N-dimethyl phosphoryl imidophosphate. A quantity of 10.6 g of dimethyl azidophosphate was added dropwise to a solution of 8.7 g of trimethyl phosphite in 10 ml of absolute ether. Three-four minutes after addition had commenced, liberation of nitrogen and heat were observed. The temperature of the mixture was kept at 15–20° by external cooling. The mixture was then boiled for 0.5 hours; the ether was driven off under vacuum and the residue was distilled. We obtained 11.2 g (51.4%) of trimethyl-N-dimethyl phosphoryl imidophosphate; the b.p. was 104–106° (0.2 mm); n_D^{20} 1.4430; d_4^{20} 1.3118. Found: C 24.3, 24.0; H 6.2, 6.3; P 24.6, 24.7%. $C_5H_{15}O_6NP_2$. Calculated: C 24.3; H 6.1; P 25.1%.

Triethyl-N-diethyl phosphoryl imidophosphate. This was obtained in a similar way to trimethyl-N-dimethyl phosphoryl imidophosphate, from 22.8 g of triethyl phosphite and 27.0 g of diethyl azidophosphate in 25 ml of ether; the yield was 42.0 g (88.5%); the b.p. was 116–117° (0.5 mm); n_D^{20} 1.4358; d_4^{20} 1.1294. Found: C 37.6, 37.7; H 8.0, 8.0; P 19.3, 19.2; N 4.7, 4.9%. $C_{10}H_{25}O_6NP_2$. Calculated: C 37.8; H 7.9; P 19.5; N 4.4%.

Triethyl-N-diethyl phosphoryl imidophosphate is a colorless liquid, soluble in organic solvents and in water.

Triethyl-N-methane sulfonyl imidophosphate. A quantity of 13.4 g of methane sulfazide was added dropwise with cooling by ice to 22.2 g of triethyl phosphite in 30 ml of ether. Liberation of nitrogen was observed immediately after addition of azide had commenced. After two distillations we obtained 22.8 g (75.8%) of triethyl-N-methane sulfonyl imidophosphate; the b.p. was 109–110° (0.2 mm); n_D^{20} 1.4500; d_4^{20} 1.2170. Found: C 32.7, 32.6; H 7.1, 7.0; P 11.8, 11.8; N 12.6, 12.6%. $C_7H_{18}O_5SNP$. Calculated: C 32.4; H 7.0; P 12.0; N 12.4%.

The action of hydrogen chloride on triethyl-N-diethyl phosphoryl imidophosphate. Dry hydrogen chloride was passed into 7.8 g of triethyl-N-diethyl phosphoryl imidophosphate at a temperature of 15–20° (external cooling). The excess hydrogen chloride and ethyl chloride were then removed under vacuum. After two distillations we obtained 3.6 g (58.4%) of diethyl-N-diethyl phosphoryl aminophosphate; the b.p. was 79–80° (0.001 mm); n_D^{20} 1.4415; d_4^{20} 1.2029. Found: C 33.2, 32.9; H 7.6, 7.4; P 21.2, 21.2%; the equivalent (thymolphthalein as indicator) was 289.0; 289.2; the mol. wt. (cryoscopically in benzene) was 611.0 (0.0198 M/kg), 618.4 (0.0427 M/kg), 590.7 (0.1362 M/kg); (cryoscopically in glacial acetic acid) 302.1; 293.8. $C_9H_{21}O_5NP_2$. Calculated: C 33.2; H 7.3; P 21.4%; the equivalent was 289.2; the mol. wt. was 289.2. The substance was a colorless viscous liquid, soluble in water but insoluble in petroleum ether. An aqueous solution reacts with a solution of soda with liberation of carbon dioxide.

The reaction of hydrogen chloride with triethyl-N-methane sulfonyl imidophosphate. The reaction was carried out as above, at 34–36°. From 2.6 g of triethyl-N-methane sulfonyl imidophosphate we obtained 1.75 g (74.5%) of diethyl-N-methane sulfonyl aminophosphate; this was recrystallized from a mixture of petroleum ether and benzene and petroleum ether and chloroform; the m.p. was 96.0–96.5°. Found: C 26.1, 26.0; H 6.1, 6.0; S 14.1, 14.0; P 13.5, 13.7%. $C_5H_{14}O_5SNP$. Calculated: C 26.0; H 6.1; S 13.9; P 13.4%.

SUMMARY

1. By reactions of dialkyl chlorophosphates and methane sulfonyl chloride with sodium azide in aqueous solution, azides of dialkyl phosphoric acids and methane sulfonic acid were obtained.
2. By reactions of triethyl phosphite with diethyl azidophosphate and methane sulfazide, triethyl-N-diethyl phosphoryl imidophosphate and triethyl-N-methane sulfonyl imidophosphate were obtained; with hydrogen chloride these compounds give diethyl-N-diethyl phosphoryl aminophosphate and diethyl-N-methane sulfonyl aminophosphate.
3. It was shown that the P=N bond in the N-acyl imidophosphates investigated is resistant to the action of water, alkylating agents, carbon bisulfide and chlorine.

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INVESTIGATION OF THE TAUTOMERISM AND GEOMETRIC
ISOMERISM OF NITROGEN-CONTAINING DERIVATIVES
OF CARBONYL COMPOUNDS

COMMUNICATION 3. POLAROGRAPHIC INVESTIGATION OF SOME SEMI- AND
THIOSEMICARBAZONES IN AQUEOUS-ALCOHOLIC SOLUTIONS

Yu. P. Kitaev, G. K. Budnikov and A. E. Arbuzov

A. E. Arbuzov Chemical Institute, Kazan Branch, Academy of Sciences, USSR

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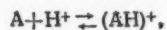
Original article submitted May 5, 1961

An important position is occupied by thiosemicarbazones [1-4] in the considerable number of compounds which have a bacteriostatic effect on *Mycobacterium tuberculosis*, which include such effective agents as tibone, sulzone, cutisone, etc. It is known that the tuberculostatic effect of thiosemicarbazones depends on the nature of the carbonyl compound; for example, thiosemicarbazones of aliphatic aldehydes and ketones, and also of alicyclic and aliphatic-aromatic ketones have a much weaker antituberculous effect than thiosemicarbazones of aromatic aldehydes [1-2].

The tuberculostatic effect of thiosemicarbazones is attributed to the $-\text{NH}-\underset{\text{C}}{\underset{\text{S}}{\text{N}}}-\text{NH}-\text{N}=\text{C}<$ group, in which the double bond of the azomethine group must be conjugated with the double $> \text{C}=\text{C} <$ bond of the carbonyl group [3]. Undoubtedly, there is a connection between the structure of the compounds and their bacteriostatic activity; the investigation of the structure of thiosemicarbazones is therefore of great theoretical and practical interest. In addition, thiosemicarbazones are used for the manufacture of certain types of photographic materials and in analytical chemistry as reagents for certain heavy-metal salts, while semicarbazones are used for the suppression of rodents [5] and as insecticides [6]. In spite of the fact that semi- and thiosemicarbazones have been the object of considerable attention for some time, the problem of the structure and state of these compounds in solution has not been finally solved. This fact stimulated us to begin a systematic investigation of the structure and conversion in solutions of representatives of these classes of compounds by the polarographic method.

Before determining the relation between polarographic data and molecular structure, we investigated the behavior of semi- and thiosemicarbazones of aliphatic-aromatic ketones at a dropping mercury electrode. The literature on the polarography of semi- and thiosemicarbazones is far from extensive. Souhay and Graizon [7] proposed a method for the polarographic determination of aldehydes and ketones in a solution of semicarbazide. On the basis of the height of the polarographic wave, these authors proposed that 2 electrons takes part in the reduction of benzophenone semicarbazone. The reduction of benzophenone semicarbazone and substituted benzophenones at a dropping mercury electrode was also investigated by Brockman and Pearson [8], who found that the effect of different substituents in the benzene ring of the ketone on the reduction of semicarbazones was negligible. Dusinsky [9] proposed a polarographic method for the determination of conteben or tibone.

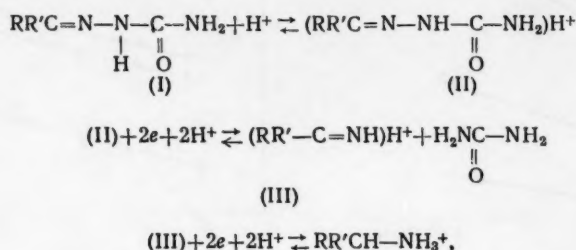
Compounds containing an azomethine group were reduced at a controlled potential by Lund [10]. He assumes that the polarographic behavior of the majority of compounds containing an azomethine group is determined in a certain pH region by the rate of recombination of molecules of substance A with hydrogen ions



the "protonized" molecule $(\text{AH})^+$ being reduced at a less negative potential than the molecule A. In neutral and weakly alkaline solutions the limiting current does not remain constant but decreases at more negative potentials

until the next electrode reaction commences. Lund explains this phenomenon by the possible variation in the structure of the $>C=N$ - double bond at the surface of the electrode, caused by the increase in the negative value of the potential, which reduces the rate of recombination of molecules with hydrogen ions. Since the number of "protonized" $(AH)^+$ molecules decreases with an increase in pH, the height of the reduction wave of the substance must also decrease, and, according to Lund, the wave must have a kinetic character. In an alkaline medium we must expect the appearance of a second wave, corresponding to the reduction of molecules A of the substance. But for the semicarbazones of benzaldehyde and p-aminoacetophenone, Lund observed only one wave in each case, the height of the wave decreasing with an increase in pH.

On the basis of an investigation of the products of reduction at a controlled potential, Lund proposes the following reduction mechanism for semicarbazones



i.e. he considers that the reduction of the $>C=N$ - bond precedes the rupture of the $-N=N-$ bond, and that the electrode reaction includes 4 electrons. However, at pH ~ 4, benzophenone semicarbazone is reduced with the participation of two electrons, and Lund could only isolate 1-benzhydryl semicarbazide. Therefore, his proposed reduction mechanism cannot be considered as finally established and a further investigation of the polarographic behavior of both semicarbazones and thiosemicarbazones is necessary.

The present communication describes the results of an investigation of acetophenone, p-chloroacetophenone and p-aminoacetophenone thiosemicarbazones and benzophenone semicarbazone. On the polarograms, both thiosemicarbazones and semicarbazones had markedly expressed minima, which disappeared with addition of agar-agar.

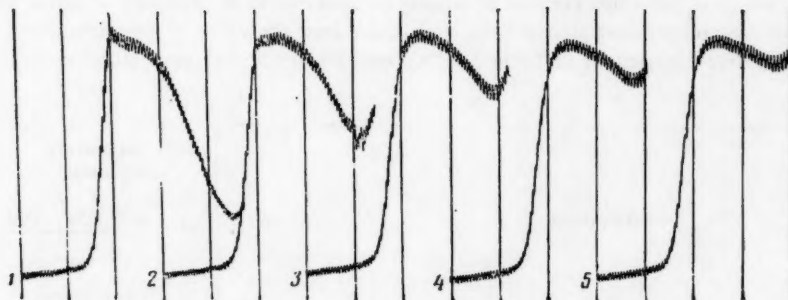


Fig. 1. Removal of the minimum on the polarogram of acetophenone thiosemicarbazone; origin of the curves 0.8 v; distance between the abscissas 200 mv; thiosemicarbazone concentration $8 \cdot 10^{-4} M$; S 1/50; agar-agar content: 1) absent; 2) 0.004%; 3) 0.01%; 4) 0.015%; 5) 0.02%.

Fig. 1 gives the polarograms of solutions of acetophenone thiosemicarbazone at pH 5.80. As may be seen from Fig. 1, after the limiting current has been reached the height of the wave decreases with an increase in the negative potential. At an agar-agar concentration of 0.02% the minimum disappears almost completely, but re-appears, however, with an increase in the pH of the solution. The observed phenomena agree with Lund's data [10]. We found that the optimum agar-agar concentration, at which the polarograms have the correct shape, is 0.04%.

An investigation of certain factors governing a diffuse current showed that the reduction of the investigated compounds is controlled by diffusion. Graphs of the relation between the wave height and the square root of the reduced height of the mercury reservoir, shown in Fig. 2, have the form of straight lines. Graphs of the relation between the value of the limiting current and temperature have a similar form (Fig. 3).

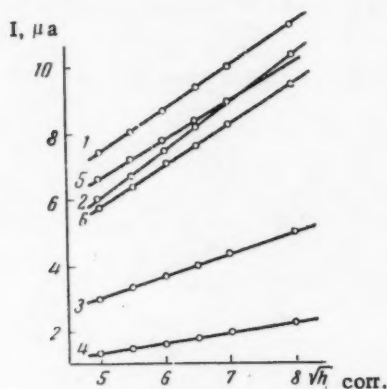


Fig. 2

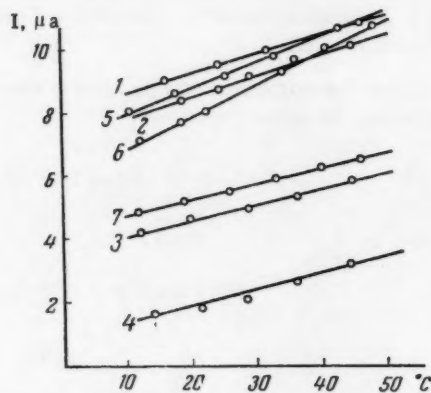


Fig. 3

Fig. 2. Relation between the value of the limiting current and the square root of the normalized height of the mercury reservoir:

1) acetophenone semicarbazone; 2) acetophenone thiosemicarbazone; 3) p-chloroacetophenone semicarbazone; 4) p-chloroacetophenone thiosemicarbazone; 5) p-aminoacetophenone semicarbazone; 6) p-aminoacetophenone thiosemicarbazone; 7) benzophenone semicarbazone.

Fig. 3. Temperature relation of the diffusion current; designation of curves, same as in Fig. 2.

It should be noted that there are practically no reports in the literature on the systematic investigation of the temperature coefficients of reduction currents of organic compounds; in the majority of cases, conclusions with regard to the nature of the electrochemical process have been drawn from the value of the temperature coefficient. The values of the temperature coefficients in Table 1, calculated for the 20-50° temperature range, also indicate that the

TABLE 1

Compound	Temperature coefficient ($i - i_{20}$) $\tau = \frac{50^\circ - 20^\circ}{i}$ 100 20° % per degree
Acetophenone semicarbazone	0.65
Acetophenone thiosemicarbazone	0.81
p-Chloroacetophenone semicarbazone	1.10
p-Chloroacetophenone thiosemicarbazone	2.60
p-Aminoacetophenone semicarbazone	0.90
p-Aminoacetophenone thiosemicarbazone	1.00
Benzophenone semicarbazone	0.90

process of reduction from weakly acid solutions at a dropping mercury electrode is controlled by diffusion; this does not agree with Lund's ideas [10] regarding the character of the reduction of compounds containing an azomethine group.

As may be seen from Table 1, the values of the temperature coefficients of the diffusion currents for thiosemicarbazones are greater than those for the corresponding oxygen analogs. Fig. 4 gives some of our polarograms, on the basis of which the relation between the diffusion currents and the height of the mercury reservoir and temperature were determined. The polarograms of the other compounds we investigated have an exactly similar appearance.

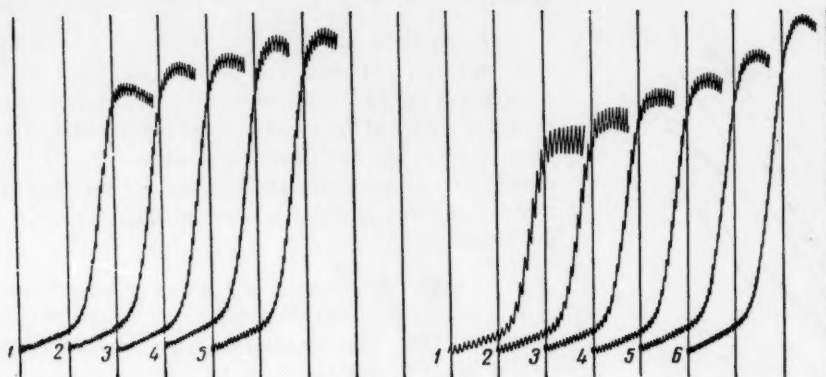


Fig. 4. Polarograms of solutions of acetophenone semicarbazone; origin of the curves 0.9 v; distance between the abscissas 200 mv; S 1/50; concentration $8 \cdot 10^{-4}$ M; pH = 5.94; the left-hand series of curves represent the temperature relation: 1 - 16.5°; 2 - 25.3°; 3 - 32.5°; 4 - 39.4°; 5 - 47.5°.

The right-hand series of curves represent the relation to the height of the reservoir:

1 - 20 cm (normalized height); 2 - 30 cm; 3 - 36 cm; 4 - 42 cm; 5 - 49 cm; 6 - 64 cm.

The linear relation between the wave height and concentration is retained in the $1 \cdot 10^{-4}$ - $8 \cdot 10^{-4}$ M concentration range (Fig. 6). An exception is formed by p-chloroacetophenone derivatives, the concentration of which could not be increased above $3 \cdot 10^{-4}$ M as a result of the low solubility. With an increase in concentration above $8 \cdot 10^{-4}$ M the increase in wave height is not strictly linear. We further established that the reduction process of the compounds investigated depends on the pH of the medium. To determine the exact value (± 2 mv) of the half-wave potential, we plotted the curves of the relation between $g \ i/i_{\alpha} - i$ and E. The angular coefficients of the slope of these straight lines ($\tan \alpha$) for the same compound at different pH values of the solution were very close to each other; the mean

TABLE 2

Compound	$\tan \alpha$	Coefficient of the slope of the straight line of the relation between $E_{1/2}$ and pH
Acetophenone semicarbazone	0.070	0.043
Acetophenone thiosemicarbazone .	0.060	0.033
p-Chloroacetophenone semicarbazone	0.054	0.074
p-Chloroacetophenone thiosemi-carbazone	0.046	0.043
p-Aminoacetophenone semicarbazone	0.045	0.087
p-Aminoacetophenone thiosemi-carbazone	0.033	0.070
Benzophenone semicarbazone	0.030	0.063

values of $\tan \alpha$ are given in Table 2. As may be seen from Table 2, the values of the coefficients of the slope indicate the irreversibility of the reduction process of the investigated compounds at a mercury dropping electrode. The value of $\tan \alpha$ for benzophenone semicarbazone (0.030) indicates a two-electron process of reduction of this compound, which is confirmed by the data of Souchay and Graizon [7].

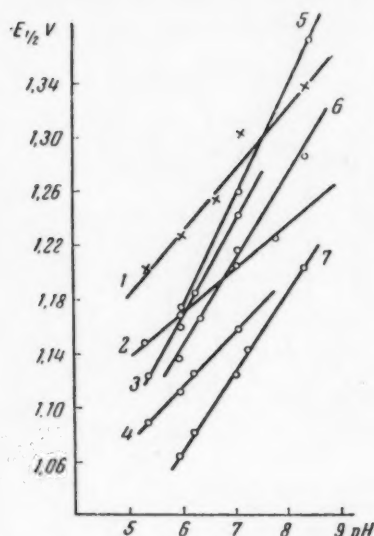


Fig. 5. Relation between $E_{1/2}$ and pH.

In the pH region investigated, the half-wave potential is a linear function of the solution pH. Fig. 5 gives the curves of the relation between the half-wave potential and the solution pH; Table 2 gives the coefficients of the slope of the straight lines obtained in this way.

A certain deviation from the linear relation between $E_{1/2}$ and pH was noted for p-chloroacetophenone derivatives at pH > 8. Some of the polarograms in Fig. 6 indicate that the wave height decreases with an increase in the pH of the solution, retaining its constant value in the narrow range of pH values of a weakly acid solution (Fig. 7). These results correspond to the experimental data of Lund [10] and Osterud [11], but the above-mentioned information does not agree with their explanation of this phenomenon.

To determine the number of electrons taking part in the reduction of the compounds investigated, we employed the method of polarographic coulometry [12]. The results of the experiments are given in Fig. 8. As may be seen from this Figure, in all cases the greater part of the points lie satisfactorily on the straight lines within the coordinated $\log I_0/I$ and t , which pass through the origin. Table 3 gives the number of electrons taking part in the reduction of one molecule of the compound, calculated from the experimental data, and the conditions under which the measurements were carried out.

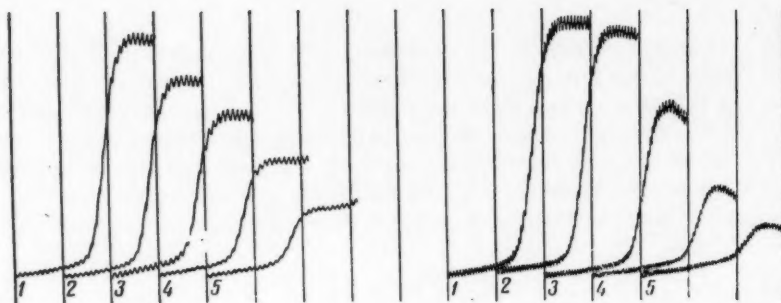
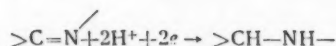


Fig. 6. Polarograms of solutions of acetophenone thiosemicarbazone; origin of the curves 0.8 v; 200 mv/absc.; S 1/50; left-hand series of curves - relation to concentration (pH 5.94); 1 - $8 \cdot 10^{-4}$ M; 2 - $6.4 \cdot 10^{-4}$ M; 3 - $4.8 \cdot 10^{-4}$ M; 4 - $3.2 \cdot 10^{-4}$ M; 5 - $1.6 \cdot 10^{-4}$ M
right-hand series of curves - relation to pH (concentration $8 \cdot 10^{-4}$ M); 1 - 5.30; 2 - 5.94; 3 - 7.05; 4 - 7.74; 5 - 8.24

From Table 3 it is evident that in all cases, two electrons per molecule of substance take part in the electrode process. This justifies the conclusion that saturation of the multiple bond of the azomethine group takes place during reduction



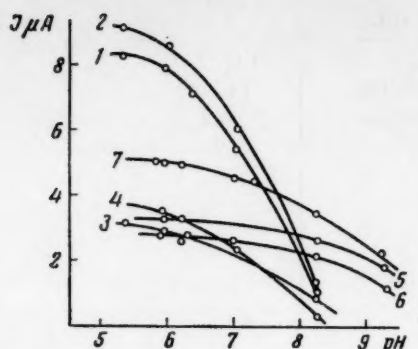


Fig. 7. Relation between wave height and the pH of the solution.

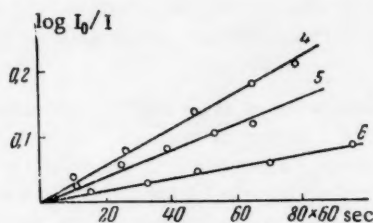
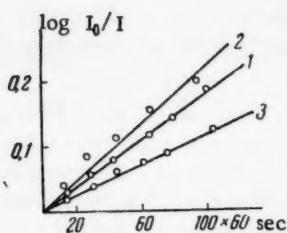


Fig. 8. Curves of the relation between $\log I_0/I$ and time. (order of the curves indicated in Table 3)

TABLE 3

No. on the graph	Compound	pH	Number of moles of the compound electrolyzed	$-E_v$ of electrolysis	Electrolysis constant, 10^{-4}	No. of electrons
1	Acetophenone semicarbazone.	5.94	$0.5 \cdot 10^{-6}$	1.40	3.48	1.90
2	Acetophenone thiosemicarbazone.	5.94	$0.5 \cdot 10^{-6}$	1.35	2.38	2.09
3	Acetophenone thiosemicarbazone.	7.0	$1.0 \cdot 10^{-6}$	1.35	5.46	1.90
4	p-Chloroacetophenone thiosemicarbazone.	5.94	$0.20 \cdot 10^{-6}$	1.30	2.30	1.80
5	Benzophenone semicarbazone	5.94	$1.0 \cdot 10^{-6}$	1.30	3.40	1.80
6	" "	—	$2 \cdot 10^{-6}$	0.90	7.10	2.10

points of the compounds used coincide with literature data. p-Aminoacetophenone semicarbazone forms an exception; an analysis of the compound recrystallized from a mixture of alcohol and water was close to the calculated values (Found: H 6.32; C 55.69%; Calculated: H 6.29; C 56.28%).

Polarographic investigation of the behavior of semi- and thiosemicarbazones in solutions. The investigation was carried out with an LR-55 polarograph of the Geirov system, with photographic recording of the polarographic curves. The current sensitivity of the galvanometer was $3.75 \cdot 10^{-9}$ amp/mm of the dial. The capillary characteristics

However, this reduction mechanism does not agree with the above - examined mechanism, proposed by Lund, in which 4 electrons take part. According to our measurements, the reduction of benzophenone semicarbazone from an aqueous-methanol solution containing hydrochloric acid and semicarbazide hydrochloride requires 2 electrons, whereas under these conditions Lund established the participation of four electrons. It is difficult to say where the cause of the discrepancy lies; nevertheless, our results indicate convincingly the two-electron reduction mechanism of the compounds investigated.

EXPERIMENTAL

The semi- and thiosemicarbazones required for the investigation were prepared by the usual methods recommended in the literature. The characteristics of the substances used in this work are given in Table 4. As may be seen from Table 4, the melting

TABLE 4

Compound	M.p., °C (expt.)	M.p., °C (lit.)	Lit. ref.
Acetophenone semicarbazone . . .	198	195-197. 203	[13. 14]
Acetophenone thiosemicarbazone	119	108. 122	[1. 14]
p-Chloroacetophenone semicarbazone	198-198.5	202-204	[14]
p-Chloroacetophenone thiosemi- carbazone	193	—	—
p-Aminoacetophenone semicarbazone	165	250	[14]
p-Aminoacetophenone thiosemi- carbazone	177-178	—	—
Benzophenone semicarbazone . . .	165-166	167	[14]

$m^2/3t^{1/6} = 2.40$; the value of the mean back pressure was approximately 1.5 cm. A saturated calomel electrode was used as the comparison electrode. The glass polarographic apparatus employed was identical to that described by Mairanovskii and Titov [15]. The temperature of the thermostatically controlled cell was kept at $25 \pm 0.1^\circ$. We used borax-phosphate solutions with a pH region of 5.30 to 9.20, which served as the background. The initial solutions of the compounds were prepared by dissolving an accurately weighed sample of the substance in methanol and their concentration was 0.01 M.

Microcoulometric investigation of semi- and thiosemicarbazones. To determine the number of electrons taking part in the reduction process, the method described in [12] by Stromberg was employed. From 0.5 to 0.6 ml of the background was introduced into the electrolyzer by means of a micropipet, the agar-agar concentration was leveled at 0.04 %; nitrogen was introduced into the background and it then operated for 20-30 minutes at the electrolysis potential. In addition to reduction from buffer solutions, to obtain a comparison with Lund's data we carried out the reduction of benzophenone semicarbazone from a 46 % aqueous methanol solution, containing 0.09 M hydrochloric acid, 0.045 % agar-agar and 0.36 % semicarbazide hydrochloride. The investigations, which were carried out under the same conditions, showed a high reproducibility of the results obtained.

SUMMARY

By means of polarographic and microcoulometric methods it was shown that the reduction of semi- and thiosemicarbazones of acetophenone, p-chloroacetophenone and p-aminoacetophenone and also benzophenone semicarbazone at a dropping mercury electrode takes place irreversibly with participation of two electrons.

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SYNTHESIS OF FLUORINATED KETONES BY MEANS OF ORGANOLITHIUM COMPOUNDS AND N, N-DIALKYL AMIDES OF FLUORINATED ACIDS

N. A. Zaitseva, E. M. Panov and K. A. Kocheshkov

L. Ya. Karpov Physicochemical Institute

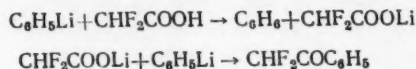
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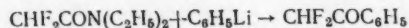
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Fluorinated ketones have not been easily available hitherto; a number of methods have been proposed for their synthesis, increasing importance being attached to those methods which employ organometallic compounds. Organomagnesium compounds in reactions with nitriles, and organozinc and organocadmium compounds with acyl chlorides of fluorinated acids give fluorinated ketones [1], in many cases with a good yield (up to 50-60 %). However, the synthesis is complicated and the initial compounds are often not readily available. In recent years, organolithium and organomagnesium compounds have been increasingly used for the synthesis of fluorinated ketones, as follows [2]:



The yield reaches 80%, but only half the organolithium compound is consumed on the formation of the ketone. This represents one of the shortcomings of the method, which may be eliminated by the use of salts of fluorinated acid [3]. We considered it of interest to find a method for preparing fluorinated ketones, convenient in the synthetic aspect, using readily available initial materials such as N,N-dialkyl amides of fluorinated acids. The reaction between organomagnesium and organolithium compounds and fluorine-free acid amides has been investigated by a number of authors [4]. Here again an excess of the organometallic compound is necessary, because part of it is decomposed by the hydrogen atoms of the amide group. Considerable heating is required to complete the reaction. With organolithium and organomagnesium compounds, N,N-dialkyl amides of acids form the corresponding aldehydes or ketones with a fairly good yield [5]. There are no data on the synthesis of fluorinated ketones by this method. The most readily available of the fluorinated acid derivatives is the diethyl amide of difluoroacetic acid [6], which is the starting point for obtaining the acid, its salts and acyl chloride.

In the present work we investigated the reaction of this amide and, to a lesser extent, the diethyl amide of trifluoroacetic acid with organosodium and organolithium compounds in various solvents at different temperatures to check the possibility of the formation of fluorinated ketones of the aliphatic, aromatic and heterocyclic series and to find the optimum conditions for their synthesis. The initial compounds were obtained by methods described in the literature. The diethyl amide of difluoroacetic acid was obtained from the acyl chloride of trifluoroacetic acid and diethylamine in ether. The diethyl amide of difluoroacetic acid reacts readily with phenyl lithium, but at room temperature a product which does not contain fluorine is formed. However, as we indicated, at a temperature of -65° in a medium of ether, ω, ω -difluoroacetophenone may be obtained with a 72 % yield



If ether is replaced by toluene the yield is reduced considerably. ω, ω -Difluoroacetophenone is also formed with phenyl sodium, but with a lower yield. Similarly, ω, ω, ω -trifluoroacetophenone is obtained from phenyl lithium and the diethyl amide of trifluoroacetic acid (yield 74 %). With thienyl lithium these amides give ω, ω -difluoroacetothienone (74 %) and ω, ω, ω -trifluoroacetothienone (39 %). From butyl lithium and the diethyl amide of

difluoroacetic acid we obtained difluoromethyl butyl ketone (32.6 %). With the diethyl amide of fluorochloroacetic acid, phenyl lithium gives ω , ω -fluorochloroacetophenone with a yield of 53 %. The initial amides are the principal admixture in the unpurified fluorinated ketone obtained by this method. Purification of the end product is simplified if excess of the organolithium compound is used. Therefore, we found that a more convenient method for obtaining fluorinated ketones was by the action of amides of fluorinated acids of the $RCONR_2$ type on organolithium compounds.

EXPERIMENTAL

Work with lithium, sodium, organolithium and organosodium compounds was carried out in an atmosphere of dry purified nitrogen. N,N-dialkyl amides of fluorinated acids were introduced into the reaction with organolithium and organosodium compounds at a temperature of 65–70°.

Preparation of ω , ω -difluoroacetophenone

a) From the diethyl amide of difluoroacetic acid and phenyl lithium in ether. A quantity of 0.1 M phenyl lithium in 240 ml of dry ether was placed in a four-necked flask equipped with a stirrer with a mercury seal, a dropping funnel, thermometer and a gas feed [7]. The reaction flask was cooled with a mixture of dry ice in alcohol to -70° and 17.2 g (0.11 M) of the diethyl amide of difluoroacetic acid [6] in 50 ml of absolute ether was added dropwise in 40 minutes at such a rate that the temperature of the mixture did not exceed -65°. The viscous mass formed was stirred at -75° for 2 hours; in this period all the phenyl lithium reacted. A Gilman color test with Michler's ketone gave a negative result. The reaction mixture was poured onto a mixture of ice and hydrochloric acid, the ethereal layer was separated, the aqueous layer was extracted three times with ether; the ethereal extract was washed with water and dried with sodium sulfate; the ether was driven off and the residue was distilled under vacuum. We obtained 13 g of a substance with a b.p. of 63–65° (10–12 mm); n_D^{20} 1.4900; the yield was 83%, calculated on the amide. According to literature data [8], ω , ω -difluoroacetophenone has a b.p. of 84–85° (26–27 mm); n_D^{20} 1.4984.

b) From the diethyl amide of difluoroacetic acid and phenyl lithium in toluene. In the apparatus described in the previous experiment we placed 12.5 g (0.12 M) of crystalline phenyl lithium [9] with a 79% C_6H_5Li content and 150 ml of dry toluene; the mixture was stirred for 15–20 minutes at room temperature and cooled to -70°. A quantity of 17.2 g (0.11 M) of the diethyl amide of difluoroacetic acid in 50 ml of dry toluene was added to the mixture in 35 minutes; it was stirred for 2 hours at -70° (Gilman test negative) and treated as in the previous experiment. The solvent was distilled under vacuum. In this case, redistillation was necessary. The yield of ω , ω -difluoroacetophenone with a b.p. of 82.5–85° (25 mm) was ~ 11.5 g (67 %).

c) From the diethyl amide of difluoroacetic acid and phenyl sodium in toluene. Phenyl sodium was obtained in the reaction flask from 11.5 g (0.5 g-atom) [7] of sodium chips, 22.5 g (0.2 M) of chlorobenzene and 150 ml of toluene; it was cooled to -70° and 15.1 g (0.1 M) of the diethyl amide of difluoroacetic acid in 15 ml of dry toluene was added in 10 minutes. The mixture was stirred for 2 hours at -70° (Gilman sample negative). The reaction mixture was decomposed with absolute alcohol and was treated as in the previous experiments. We obtained 4.5 g (29 %) of ω , ω -difluoroacetophenone.

Preparation of Difluoro - α - Acetothienone

We obtained α -thienyl lithium from 0.186 M of butyl lithium in 280 ml of ether and 0.126 M of thiophene [10]. The butyl lithium was first filtered from unreacted lithium and its concentration was determined by the usual method. An equivalent amount of the diethyl amide of difluoroacetic acid in an equal volume of ether was added (about one hour) to the suspension of thienyl lithium at a temperature below -65°. The reaction mixture was stirred for about another hour at this temperature and was poured into a mixture of ice and hydrochloric acid. After the usual treatment we obtained a substance with a b.p. of 77–80° (11 mm) with a yield of ~ 75 % of the theoretical. The synthesis may be carried out without preliminary filtration and analysis of butyl lithium (taking into account its possible yield). In one of the experiments, from 1.29 M of lithium, 0.555 M of butyl chloride, 0.476 M of thiophene and 0.476 M of the diethyl amide of difluoroacetic acid we obtained 57 g of a product with a b.p. of 80° (13 mm), i.e. 74 % of the theoretical. In this case, care is required when decomposing the reaction mixture (lumps of unreacted lithium remain). Found: F 23.00, 23.25 %. $C_6H_4OF_2S$. Calculated: F 23.43 %.

Preparation of ω , ω , ω -Trifluoroacetophenone

a) From the diethyl amide of trifluoroacetic acid and phenyl lithium in ether. A quantity of 10 g (0.06 M) of the diethyl amide of trifluoroacetic acid in 35 ml of ether was added to 0.06 M of phenyl lithium in 64 ml of ether. After redistillation we obtained 8 g (74 %) of the substance with a b.p. of 66–68° (37 mm); n_D^{20} 1.4578. According to literature data [8], ω , ω , ω -trifluoroacetophenone has a b.p. of 66–67° (37 mm); n_D^{20} 1.4576.

b) From the diethyl amide of trifluoroacetic acid and phenyl lithium in toluene. A quantity of 14.5 g (0.086 M) of the diethyl amide of trifluoroacetic acid in 50 ml of toluene was added gradually to 8 g (0.075 M) of crystalline phenyl lithium (with a C_6H_5Li content of 79 %) in 150 ml of toluene. After the mixture had been stirred (at -75°) for 2.5 hours, a Gilman test gave a positive result. After the usual treatment the product obtained was distilled. We obtained 7.1 g (54.5%) of ω, ω, ω , -trifluoroacetophenone.

Preparation of ω, ω, ω -Trifluoroacetothienone.

A quantity of 15 g (0.09 M) of the diethyl amide of trifluoroacetic acid in 15 ml of ether was added to the α -thienyl lithium obtained from 0.146 M of butyl lithium in 110 ml of ether and 11.7 g (0.14 M) of thiophene [10]. The reaction mixture was stirred for an hour and left overnight at -80° . We obtained 6.3 g (39 %) of the product, with a b.p. of 67° (23-24 mm). Found: F 31.10 %. $C_6H_3OF_3S$. Calculated: F 31.60%.

Preparation of the Diethyl Amide of Trifluoroacetic acid.

A quantity of 82 g (115.5 ml) of diethylamine in 180 ml of absolute ether was placed in a round-bottomed flask equipped with a stirrer with a mercury seal, a reflux condenser, dropping funnel and thermometer, and a solution of 60 g of the acyl chloride of trifluoroacetic acid in 100 ml of absolute ether (cooled by dry ice) was added at 0° . The white precipitate was filtered at the pump, the ethereal layer was washed twice with water and dried with sodium sulfate. The ether was driven off and the residue was distilled under vacuum. We obtained 36 g (47.4 %) of the diethyl amide of trifluoroacetic acid with a b.p. of $74-75^\circ$ (43 mm).

Preparation of ω, ω -Fluorochloroacetophenone.

A quantity of 150 ml (0.158 M) of an ethereal solution of phenyl lithium was placed in the apparatus and 23.8 g (0.142 M) of the diethyl amide of fluorochloroacetic acid [6] in 70 ml of absolute ether was added over a period of one hour. The mixture was stirred for a further 2 hours at -70° . The Gilman reaction was negative. The light-brown transparent liquid obtained was poured with vigorous stirring onto a mixture of ice and hydrochloric acid. We obtained 13 g (53 %) of the substance, with a b.p. of 91° (11 mm). Found: F 11.78 %. C_8H_6OFCl . Calculated: F 11.02%.

Preparation of Difluoromethyl Butyl Ketone from the Diethyl Amide of Difluoroacetic Acid and Butyl Lithium.

A quantity of 40.8 g (0.27 M) of the diethyl amide of difluoroacetic acid in 60 ml of absolute ether was added dropwise to the butyl lithium obtained from 33 g (0.36 M) of butyl chloride and 5 g (0.72 g-atom) of lithium. Addition of the diethyl amide took ~ 2 hours; the reaction mass was then stirred for another hour at the same temperature. The Gilman reaction was negative. The contents of the flask were poured through a metal sieve into a mixture of ice and hydrochloric acid and treated as usual. We obtained 12 g (32.6%) of product with a b.p. of $104-110^\circ$; after redistillation the b.p. was $111-112^\circ$. Found: F 28.30, 28.20%. $C_6H_{10}OF_2$. Calculated: F 27.93%.

SUMMARY

1. A convenient method was found for the synthesis of fluorinated ketones from organolithium compounds and N, N-dialkyl amides of fluorinated acids.

2. ω, ω, ω -trifluoro- α -acetophenone, ω, ω -difluoro- α -acetothienone and difluoromethyl butyl ketone were synthesized for the first time.

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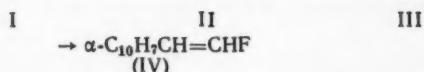
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THE SYNTHESIS OF VINYL NAPHTHALENES WITH FLUORINATED SIDE CHAINS

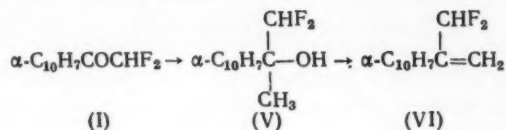
G. V. Kazennikova, T. V. Talalaeva, A. V. Zimin, A. P. Simonov
and K. A. Kocheshkov

L. Ya. Karpov Physicochemical Institute
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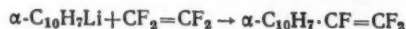
Continuing the investigation of new fluorinated monomers of the aromatic series [1], we developed a method for the synthesis of β -fluoro- α -vinyl naphthalene and α -difluoromethyl- α -vinyl naphthalene. The starting point for the synthesis of β -fluoro- α -vinyl naphthalene was α -difluoromethyl naphthyl ketone, obtained with a ~ 50% yield by condensation of α -naphthyl lithium with the diethyl amide of difluoroacetic acid [2] at -75° . This ketone was reduced with sodium borohydride to the corresponding carbinol. The yield of difluoromethyl- α -naphthyl carbinol was then converted by thionyl chloride to α -chloro- β , β -difluoroethyl naphthalene with a ~ 70% yield. By removal of chlorine and fluorine by the action of zinc in a medium of acetamide [1], we obtained an ~ 80% yield of β -fluoro- α -vinyl naphthalene.



By condensing α -difluoromethyl naphthyl ketone with methyl lithium at -20° we obtained α -naphthyldifluoromethylmethyl carbinol with an 88% yield. By the action of phosphorus pentoxide in benzene we then obtained α -difluoromethyl- α -vinyl naphthalene with a 45-50% yield



For the synthesis of α -perfluorovinyl naphthalene, we condensed tetrafluoroethylene with α -naphthyl lithium



Pure, anhydrous tetrafluoroethylene was passed into a dilute ethereal solution of α -naphthyl lithium at -75° . The yield of α -perfluorovinyl naphthalene reaches 10-15%. When the reaction was carried out under conditions of slow addition of an α -naphthyl lithium solution to excess tetrafluoroethylene at -75° , the yield fell to 3-5%. The infrared absorption spectra of β , β -difluoro- α -chloro-1-ethyl naphthalene, β -fluoro- α -vinyl naphthalene and perfluoro- α -vinyl naphthalene in the $650\text{-}2000\text{ cm}^{-1}$ region were investigated; these are very difficult to interpret as a result of their complexity, particularly in the region from $650\text{ to }1400\text{ cm}^{-1}$. The Table gives the frequencies of the strongest absorption bands (in cm^{-1}), the allocation of which was only approximate. In the $1000\text{-}1400\text{ cm}^{-1}$ region the strongest absorption is evidently due to C-F valence vibrations. In the $650\text{-}1000\text{ cm}^{-1}$ region, where nonplanar deformation vibrations of CH rings occur, there is a very strong ~ 790 cm^{-1} band, characteristic of α -monosubstituted naphtha-

TABLE

Vibration, cm ⁻¹ .	$\alpha\text{-C}_{10}\text{H}_7\text{CHCl-CHF}_2$	$\alpha\text{-C}_{10}\text{H}_7\text{C}^+\text{H-CH}$	$\alpha\text{-C}_{10}\text{H}_7\text{CF=CF}_2$
C=C valence vibration	—	1663 (v,s)	1787 (v,s)
Skeletal vibrations of the rings	1596 (s) 1508 (s)	1598 (m) 1515 (m)	1602 (m) 1516 (s)
C-F valence vibration	1377 (v,s) 1352 (s)		1322 (s) 1295 (v,s) 1255 (v,s) 1193 (v,s) 1142 (v,s)
	1209 (s) 1137 (v,s) 1113 (v,s) 1063 (v,s) 1027 (s)	1168 (s) 1100 (v,s) 1080 (s) 1030 (m)	1093 (v,s) 1055 (s)
Nonplanar deformation vibration of CH rings	949 (s) 868 (s) *755 (v,s)	910 (s) 790 (v,s) 773 (v,s)	944 (v,s) 795 (v,s) 768 (v,s)

* Center of a very strong wide band.

lenes [3]. The Table shows that displacement of the frequency of the C=C valence vibration in the direction of higher frequencies occurs as a result of substitution of the hydrogen atoms of the vinyl group by fluorine.

EXPERIMENTAL

Preparation of difluoromethyl- α -naphthyl ketone (I). α -Naphthyl lithium was obtained in the usual way from 330 ml of an ethereal solution of *n*-butyl lithium (21.1 g, 0.33 M) and 68 g (0.33 M) of α -bromonaphthalene, diluted with 100 ml of ether with stirring, in an atmosphere of argon, at a temperature of $\sim 20^\circ$. The reaction was carried out in a low-temperature condensation apparatus (capacity 1 liter). The reaction mixture was cooled to -78° (with a mixture of alcohol and dry ice) *. A quantity of 40.5 g (0.3 M) of the diethyl amide of difluoroacetic acid [2] was added with vigorous stirring and a temperature of $\sim -75^\circ$. It was stirred for another hour and decomposed by carefully pouring into a mixture of ice and dilute hydrochloric acid. After usual treatment and two distillations under vacuum we obtained difluoromethyl- α -naphthyl ketone with a b.p. of $110\text{--}115^\circ$ (2 mm); n_D^{20} was 1.5995; the yield was 45–55%. For analysis, the substance was distilled under high vacuum. n_D^{20} 1.5981. Found: C 69.96, H 3.92; F 18.27%. $\text{C}_{12}\text{H}_9\text{F}_2\text{O}$. Calculated: C 69.90; H 3.88; F 18.45%.

Preparation of α -naphthyl difluoromethyl carbinol (II). A quantity of 4 g of sodium borohydride, dissolved in 16.5 ml of water, and 3 ml of 10% caustic soda was placed in an ordinary three-necked flask (capacity 150 ml) with a stirrer, reflux condenser and dropping funnel. We added 26 g of difluoromethyl- α -naphthyl ketone in an equal volume of methyl alcohol (with vigorous stirring). During the period of addition the temperature rose to 46° . When all the material had been added, the mixture was stirred for a further 3 hours at 35° , and was then decomposed by pouring into 200 ml of water; the liberated oil was extracted with ether, washed dried and distilled. After two distillations under vacuum we obtained 22.3 g of α -naphthyl difluoromethyl carbinol with a b.p. of 140° (2 mm); n_D^{20} 1.5910; the yield was 83.2%. Found: C 70.10; H 4.95; F 19.93%. $\text{C}_{12}\text{H}_9\text{F}_2\text{O}$. Calculated: C 68.26; H 4.80; F 18.26%.

Preparation of α -chloro- β , β -difluoroethyl naphthalene (III). A mixture of 17 g of α -naphthyl difluoromethyl carbinol and 40 g of thionyl chloride (large excess) was stirred for 1 hour in an ordinary apparatus at $80\text{--}85^\circ$. The mixture was then cooled to room temperature and decomposed by pouring into ice water. The liberated oil was

* A Phenoplast (polystyrene) vessel with ~ 100 mm thick walls may be conveniently used instead of a Dewar flask for cooling with a mixture of alcohol and dry ice.

washed once with water and was then extracted with benzene. The benzene solution was washed with a 20% soda solution and cold water, dried and distilled. We obtained 12.5 g (69.4%) of α -chloro- β , β -difluoroethyl naphthalene, with a b.p. of 111° (2 mm); n_D^{20} was 1.5890. After recondensation under high vacuum, n_D^{20} was 1.5901 and n_D^{25} 1.5878. Found: Cl 15.30; F17.02%. $C_{12}H_9F_2Cl$. Calculated: Cl 15.67; F 16.75%.

Preparation of β -fluoro- α -vinyl naphthalene (IV). We placed 28 g of α -chloro- β , β -difluoroethyl naphthalene, 70 g of acetamide, 0.6 g of copper powder and 12 g of active zinc dust (freshly distilled) in a 100 ml round-bottomed flask. The reaction mass was thoroughly mixed and was then heated gradually to 150° and kept for 2 hours at this temperature. The mixture was decomposed by pouring into ice water, acidified with 10 ml of sulfuric acid. After the usual treatment and distillation under vacuum we obtained 15.5 g (68 %) of β -fluoro- α -vinyl naphthalene; the b.p. was 92-93° (2 mm); n_D^{20} 1.6220. The substance is a mobile liquid with a faint odor of naphthalene; it adds bromine readily. Found: C 83.92; 83.95; H 5.59; 55.5; F 10.30; 10.04 %. $C_{12}H_9F$. Calculated: C 83.72; H 5.23; F 11.04%.

Preparation of α -naphthyl difluoromethyl methyl carbinol (V). In a low-temperature condensation apparatus we placed 200 ml of an ethereal solution of methyl lithium obtained from methyl chloride and lithium (3 g of CH_3Li ; 0.14 M), it was diluted with 150 ml of absolute ether and cooled to -25°. A quantity of 28.84 g (0.14 M) of difluoromethyl naphthyl ketone in 100 ml of absolute ether was added in 1.5 hours at a temperature of not more than -20°. The mixture was kept at this temperature for a further 2 hours until the reaction was completed (negative reaction with Michler's ketone). The mixture was decomposed by pouring into ice and dilute hydrochloric acid; it was extracted with ether, the ethereal solution was washed with a 2% solution of soda and water, dried, and distilled under vacuum twice; the b.p. was 120° (2.5 mm). We obtained 27.6 g (88%) of compound (V). The carbinol is a viscous, slightly yellowish liquid, crystallizing readily at room temperature.

Preparation of α -difluoromethyl- α -vinyl naphthalene (VI). A mixture of 11.1 g of α -naphthyl difluoromethyl carbinol (0.05 M), 3.55 g of phosphorus pentoxide (0.025 M), 100 ml of benzene, and 0.3 g of active copper powder were placed in an ordinary flask with a reflux condenser in an atmosphere of nitrogen and heated to boiling for 5 hrs. After the usual treatment and two distillations under vacuum we obtained 4.8 g of α -difluoromethyl- α -vinyl naphthalene (46 %); the b.p. was 105° (2 mm), n_D^{20} was 1.5830. For analysis, the substance was recondensed under high vacuum; n_D^{20} was 1.5833. Found: C 76.71; H 4.91; F 18.45%. $C_{13}H_{10}F_2$. Calculated: C 76.40; H 4.90; F 18.72%.

SUMMARY

Methods for the synthesis of β -fluoro- α -vinyl naphthalene and α -difluoromethyl- α -vinyl naphthalene were developed.

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THE REACTION OF ETHYLENE WITH TRICHLORO- AND TETRACHLOROETHYLENE

A. B. Belyavskii and R. Kh. Freidlina

Institute of Heteroorganic Compounds, Academy of Sciences, USSR

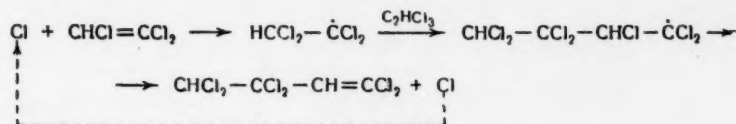
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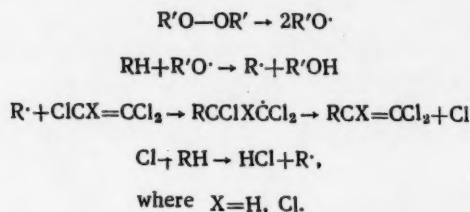
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When trichloroethylene is heated in the presence of peroxides it does not polymerize, but forms a dimer: $\text{CHCl}_2\text{CCl}_2\text{CH}=\text{CCl}_2$. One of the causes of this reaction trend is the fairly long life of the intermediate radicals with the $>\text{CCl}-\text{CCl}_2$ group, which are stabilized with the removal of chlorine. The following system was proposed for the dimerization of trichloroethylene [1]:



Tetrachloroethylene does not polymerize, even when heated to 200° at 30,000 atm [2].

In contrast to perfluoroethylene, the reaction of trichloro- or tetrachloroethylene with saturated hydrocarbons in the presence of peroxides is not of the telomerization type, with formation of compounds with the structure $\text{C}_n\text{H}_{2n+1}(\text{CHClCCl}_2)_x\text{H}$ and $\text{C}_n\text{H}_{2n+1}(-\text{CCl}_2)_{n+1}(-\text{CCl}_2-\text{CCl}_2-)_x\text{H}$, but of the condensation type, being formed the unsaturated compounds $\text{C}_n\text{H}_{2n+1}\text{CH}=\text{CCl}_2$ and $\text{C}_n\text{H}_{2n+1}\text{CCl}=\text{CCl}_2$; the following system was proposed for these reactions [3]:



The reaction of trichloro- and tetrachloroethylene with ethylene is described briefly in the patent [4]. The author assumes that a telomerization reaction takes place in both cases. However, from a mixture of the products obtained by reacting ethylene with tetrachloroethylene in the presence of peroxides and at a pressure of 95 atm the author could isolate only one product: 1, 1, 2, 6-tetrachlorohexene-1. In the case of the reaction with trichloroethylene at a pressure of 850-1005 atm, individual products were not isolated. From the complex mixture obtained by reacting ethylene with tetrachloroethylene at 140° and 50 atm in the presence of tertiary butyl peroxide and water, we isolated individual lower telomers: $\text{Cl}(\text{CH}_2\text{CH}_2)_n\text{CCl}=\text{CCl}_2$, where $n = 1, 2, 3$. In the present work we continued the investigation of this reaction, and also investigated the reaction of ethylene with trichloroethylene and some chemical conversions of the telomers obtained.

When the reaction products of ethylene and tetrachloroethylene were distilled, we noted that the fraction boiling higher than 1, 1, 2, 8-tetrachlorooctene-1 has an unexpectedly high specific gravity. From this fraction, by careful distillation we obtained a compound which was found to be 1, 1, 2, 5, 5, 6, 6, 6-octachlorohexene-1; its structure was proven by the following reactions:

EXPERIMENTAL

Telomerization of ethylene with trichloroethylene. A quantity of 197 g of trichloroethylene was placed in a 0.5 liter stainless steel vibrating autoclave; the air was displaced from the autoclave by nitrogen and ethylene was introduced until the pressure was 60 atm. The mixture was heated to 260-270°; at this temperature the pressure was reduced from 290 to 150 atm. The products from a series of analogous experiments were combined. We took 1700 g of these products for distillation. The following were obtained: 1) trichloroethylene, 958 g; 2) 1, 1, 4-trichlorobutene-1, 169 g; the b.p. was 69.5° (24 mm); n_D^{20} 1.4910; d_4^{20} 1.3190. Found MR 34.95. $C_4H_5Cl_3$. Calculated MR 34.80. Found: C 31.30, 31.55; H 3.45, 3.33; Cl 65.56, 65.53%. Calculated: C 30.13; H 3.16; Cl 66.76%. 3) 1, 1, 6-Trichlorohexene, 118 g; the b.p. was 89° (11 mm); n_D^{20} 1.4870; d_4^{20} 1.2258. Found MR 44.00. $C_6H_9Cl_3$. Calculated MR 44.04. Found: C 37.63; 37.59; H 4.43, 4.51; Cl 56.42, 56.11%. Calculated: C 38.43; H 4.83; Cl 56.72%. The residue of high telomers and the intermediate fractions were not investigated.

Hydrolysis of 1, 1, 4-trichlorobutene-1. A mixture of 1, 1, 4-trichlorobutene-1 and 110 g of 93% H_2SO_4 was stirred at a temperature of 65° until liberation of HCl had ceased; as a result of ordinary treatment and distillation we obtained 7g of the initial substance and 17 g of ω -chlorobutyric acid; the b.p. was 86° (2 mm); n_D^{20} 1.4512; d_4^{20} 1.2246. Found MR 26.96. $C_4H_7O_2Cl$. Calculated MR 27.07. The m.p. of the anilide was 68°. Found: C 60.77, 60.86; H 6.23, 6.03; Cl 18.05, 18.16%. $C_{10}H_{12}NOCl$. Calculated: C 60.76; H 6.11; Cl 17.93%.

Hydrolysis of 1, 1, 6-trichlorohexene-1. Under conditions similar to the previous experiment we obtained a 66% yield (of the theoretical) of ω -chlorocaproic acid from 50 g of 1, 1, 6-trichlorohexene-1 by treatment with 200 g of H_2SO_4 ; the b.p. was 100.5° (1.5 mm); the m.p. was 23°. Found: C 47.27, 47.40; H 7.30, 7.36; Cl 24.42; 24.35%. $C_6H_{11}O_2Cl$. Calculated: C 45.74; H 7.36; Cl 23.54%. Anilide: m.p. 84°. Found: C 63.85, 63.80; H 7.19; 7.02; Cl 15.99, 15.60%. $C_{12}H_{16}NOCl$. Calculated: C 63.84; H 7.14; Cl 15.71%. Methyl ester: b.p. 97° (15 mm); n_D^{20} 1.4425; d_4^{20} 1.0627. Found MR 40.96. $C_7H_{13}O_2Cl$. Calculated MR 41.05. Found: C 50.80, 50.81; H 7.88, 7.84; Cl 21.34, 21.44%. Calculated: C 51.06; H 7.95; Cl 21.54%.

Bromination of 1, 1, 4-trichlorobutene-1. An equimolecular amount of a solution of bromine in 15 ml of carbon tetrachloride was added to a solution of 32 g (0.2 M) of 1, 1, 4-trichlorobutene-1 in 15 ml of carbon tetrachloride. After usual treatment with a solution of soda, drying over calcium chloride and distillation we obtained 51 g (80% of the theoretical) of 1, 1, 4-trichloro-1, 2-dibromobutane; the b.p. was 95° (4 mm); n_D^{20} 1.5640; d_4^{20} 2.0496. Found MR 50.79. $C_4H_5Br_2Cl_3$. Calculated: MR 50.80. Found: C 15.53, 15.24; H 1.64, 1.59; Hal 83.19, 84.45%. Calculated: C 15.10; H 1.56; Hal 83.47%.

Hydrolysis of 1, 1, 4-trichloro-1, 2-dibromobutane by anhydrous nitric acid. We added 80 ml of nitric acid (sp. gravity 1.52) dropwise to 58 g of 1, 1, 4-trichloro-1, 2-dibromobutane with stirring at a temperature of 50-60°. When addition of nitric acid had been completed, the mixture was stirred for a further two hours at this temperature and was then diluted with water. The organic oil was extracted with chloroform. The acid products were separated, dried over $CaCl_2$ and distilled. We obtained 22 g of acid; the b.p. was 105° (4 mm); n_D^{20} 1.5100, d_4^{20} 1.7224. Found: MR 34.38. $C_4H_5O_2BrCl$. Calculated MR 34.84. Found: C 23.79, 23.58; H 3.02, 3.05; Hal 56.54, 56.44%. Calculated: C 23.84; H 3.00; Hal 57.26%. Anilide: m.p. 103° (from benzene). Found: C 43.78, 43.72; H 4.23, 4.18; Hal 41.67, 41.82%. Calculated: C 43.42; H 4.01; Hal 41.79%.

Chlorination of 1, 1, 2, 4-tetrachlorobutene-1. A mixture of 63 g of 1, 1, 2, 4-tetrachlorobutene-1 and 1.15 g of $FeCl_3$ was saturated with chloroform, with stirring at a temperature of 0-2°. In all, 20 g of chlorine was absorbed. The reaction mixture was treated with a solution of soda and dried over calcium chloride. Distillation gave the following fractions: fraction I, up to 67° (1 mm), 20 g (initial substance); fraction II, 67° (0.5 mm), 36 g; residue 4 g. The substance of fraction (II) had the following constants: d_4^{20} 1.6489; n_D^{20} 1.5280. Found MR 49.46. $C_4H_4Cl_6$. Calculated MR 49.87. Found: C 18.26, 18.15; H 1.51, 1.33; Cl 80.25, 80.35%. Calculated: C 18.14; H 1.50; Cl 79.72%.

1, 1, 2, 5, 5, 6, 6-Octachlorohexene-1. The reaction between ethylene and tetrachloroethylene was carried out as described previously [5]. From the products of several analogous experiments we collected a fraction with a b.p. of 120-130° (2 mm). By careful fractionation of this product in a column we obtained octachlorohexene with an m.p. of 32° (from acetone). Found: C 20.45, 20.46; H 1.04, 1.01; Cl 76.53, 76.72%. $C_8H_4Cl_8$. Calculated: C 20.04; H 1.12; Cl 78.53%.

2, 2, 5, 5, 6, 6-Heptachlorocaproic acid. A quantity of 30 ml of anhydrous nitric acid (sp. gravity 1.515) was added dropwise with stirring to 27 g (0.075 M) of 1, 1, 2, 5, 5, 6, 6-octachlorohexene-1. The reaction was exothermic. When all the nitric acid had been added, the mixture was heated for 2 hours at 55-60°. A copious pre-

precipitate was deposited from the reaction mixture, cooled to room temperature. The precipitate was filtered, dried and recrystallized. After two recrystallizations from benzene we obtained 23 g of the substance with an m.p. of 162°. Found: C 20.45, 20.46; H 1.31, 1.38; Cl 68.85, 68.97%. $C_6H_5Cl_7O_2$. Calculated: C 20.16; H 1.39; Cl 69.46%.

1, 1, 2, 5, 6, 6-Hexachlorohexadiene-1, 5. A quantity of 15 g of octachlorohexene was added with stirring to 8 g of zinc (activated by heating with 0.1 ml of glacial acetic acid and 0.5 ml of hydrobromic acid) in 30 ml of alcohol. The reaction was accompanied by liberation of heat. The chloroform extract was washed with dilute hydrochloric acid, dried over $CaCl_2$ and, after the chloroform had been driven off, it was distilled from the flask with a fishbone-type fractionating column. We obtained 9 g of the substance (75% of the theoretical); the b.p. was 83° (1 mm); n_D^{20} 1.5410; d_4^{20} 1.5548. Found MR 58.38. $C_6H_4Cl_6$. Calculated MR 58.17. Found: C 25.59, 25.47; H 1.39, 1.53%. Calculated: C 24.95; H 1.51%.

2, 2, 5, 5-Tetrachloroadipic acid. A mixture of 6 g of heptachlorohexadiene (see previous experiment) and 8 ml of anhydrous nitric acid was heated at 55-60°, with stirring, for 5 hours. With cooling to room temperature, a precipitate was deposited (3, 5 g). This was filtered, washed with benzene and ether and dried under vacuum, the m.p. was 198°. Found: C 25.27, 25.46; H 2.05, 2.14%. $C_6H_6Cl_4O_4$. Calculated: C 25.38; H 2.13%.

The action of nitric acid on the polymer obtained from 1, 1, 2-trichlorobutadiene-1, 3. A sample of polymer (1 g) was covered with 10 ml of anhydrous nitric acid. After it had been allowed to stand for two days at room temperature the polymer had dissolved almost completely in the acid; the residue dissolved when the reaction mass was heated for 2 hours at 55-65°. The solution was diluted with water, the precipitate was filtered, washed thoroughly and dried in a vacuum desiccator over caustic potash. Found: C 26.87, 26.87; H 1.81, 1.83; N 3.94; Cl 40.20, 40.15%. $C_8H_7O_8ClN$. Calculated: C 27.06; H 1.98; N 4.41; Cl 39.95%.

SUMMARY

- 1, 1, 4-trichlorobutene-1 and 1, 1, 6-trichlorohexene-1 were isolated from a mixture of the products obtained by thermal polymerization of trichloroethylene and ethylene.
- As a result of the telomerization of ethylene with tetrachloroethylene, together with tetrachloroalkenes with the structure $Cl(CH_2CH_2)_nCCl=CCl_2$ more highly chlorinated products are also obtained, from which it was possible to isolate 1, 1, 2, 5, 5, 6, 6, 6-octachlorohexene-1.

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STEREOCHEMISTRY OF HETEROCYCLIC COMPOUNDS

ARTICLE 5. POSSIBLE CONFIGURATION OF STEREOISOMERS OF

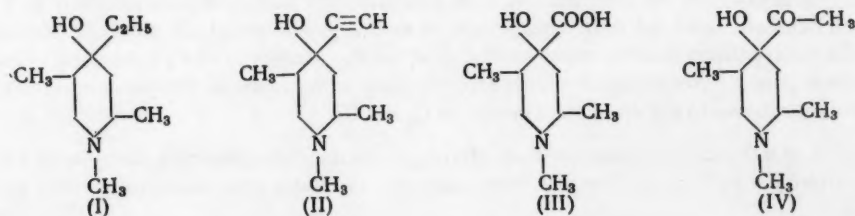
1, 2, 5-TRIMETHYL-4-ETHYNYL-4-PIPERIDINOL AND THEIR CONVERSION PRODUCTS

N. I. Shvetsov, B. V. Unkovskii, I. A. Mokhir, and V. F. Kucherov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences,
USSR; M. V. Lomonosov Institute of Fine Chemical Technology
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In many works devoted to the synthesis of various derivatives of 1, 2, 5-trimethyl-4-piperidone the formation of geometrical isomers was frequently observed, whose configuration remained unknown until recently. The earlier-proposed method of attacking the problem of the configuration of piperidone derivatives made it possible, on the basis of several assumptions, to express opinions on the possible steric structure of all four geometrical isomers of 1, 2, 5-trimethyl-4-phenyl-4-piperidinol [1] and certain other stereoisomeric compounds of this series [2]. It seemed to us expedient to employ this route of proof in order to gain some idea of the possible configuration of stereoisomeric derivatives of 1, 2, 5-trimethyl-4-piperidone, obtained earlier; this is the subject of the present article.

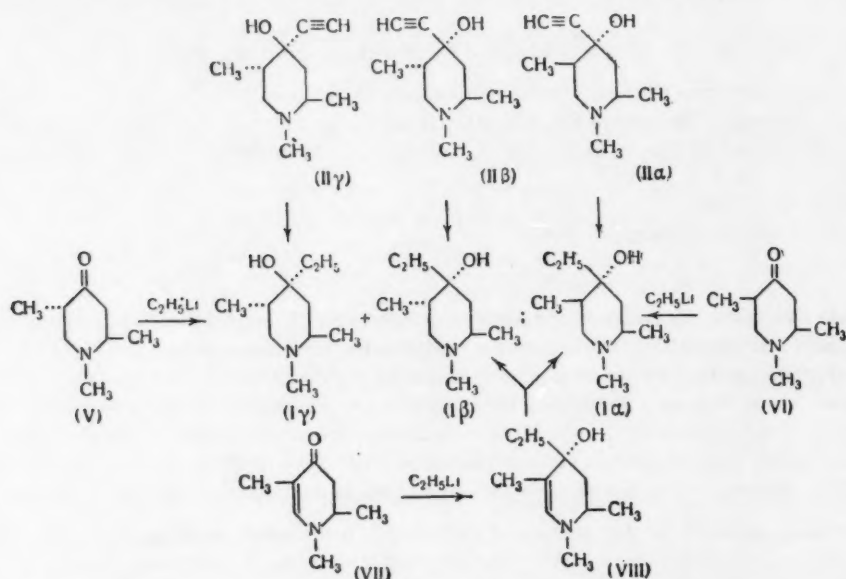
One of the starting materials for the synthesis of various 1, 2, 5-trimethylpiperidine derivatives consists of geometrical isomers of 1, 2, 5-trimethyl-4-ethynyl-4-piperidinol (II) [3]; on the basis of these isomers, as was established earlier [4], it is easy to prepare the corresponding stereoisomeric hydroxy acids (III) and hydroxy ketones (IV), whose configuration is the same as that of the original acetylenic alcohols



Before taking up the problem of the possible configuration of stereoisomeric 1, 2, 5-trimethyl-4-ethynyl-4-piperidinols (II), we had to try to determine the steric structures of the corresponding 1, 2, 5-trimethyl-4-ethyl-4-piperidinols (I), formed on catalytic hydrogenation of the original acetylenic alcohols. For this purpose, using methods developed earlier, we synthesized isomeric 1, 2, 5-trimethyl-4-ethyl-4-piperidinols (I) by two different routes; based on this, we drew conclusions on their possible configuration. It was found that in the reaction of trans-piperidone (V) with ethyllithium there are formed only two isomeric 1, 2, 5-trimethyl-4-ethyl-4-piperidinols, (γ) and (β), which have a trans-arrangement of methyl groups and must be C_4 epimers. In a similar reaction with a piperidone mixture consisting mainly of the cis-isomer (VI), we isolated not only these two alcohols, but also a third isomer of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol (I α) which, according to the method of its preparation, must have a cis-arrangement of the methyl groups at C_2 and C_5 .

In order to gain an idea of the possible configuration of substituents on C_4 in isomers of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol (γ , β , α), we studied the catalytic hydrogenation of 1, 2, 5-trimethyl-4-ethyl- Δ^5 -dehydro-4-piperidinol (VIII), obtained in the reaction of ethyllithium with the earlier-described [1] 1, 2, 5-trimethyl- Δ^5 -dehydro-4-piperidone (VII). In analogy with certain data obtained earlier [1, 5] we assumed that 1, 2, 5-trimethyl-4-ethyl- Δ^5 -dehydro-4-piperidinol (VIII) had the energetically more favorable cis-arrangement of the alkyl substituents on C_2 and C_4 . According to this its catalytic hydrogenation should lead to isomeric 1, 2, 5-trimethyl-4-ethyl-4-pipe-

ridinols having the same configuration at C₄ but differing by the cis- or trans-arrangement of the methyl groups. We showed that the hydrogenation of 1, 2, 5-trimethyl-4-ethyl- Δ^5 -dehydro-4-piperidinol (VIII) gives a mixture of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol α - and β - isomers and on the basis of the assumptions made earlier therefore, these products may be assigned the configurations corresponding to Formulas (I β) and (I α). The third of the isomers which we prepared, being a C₄ epimer of (I β), can have only one configuration (I γ), since it is obtained by ethyl-lithium synthesis from trans-piperidone (V).



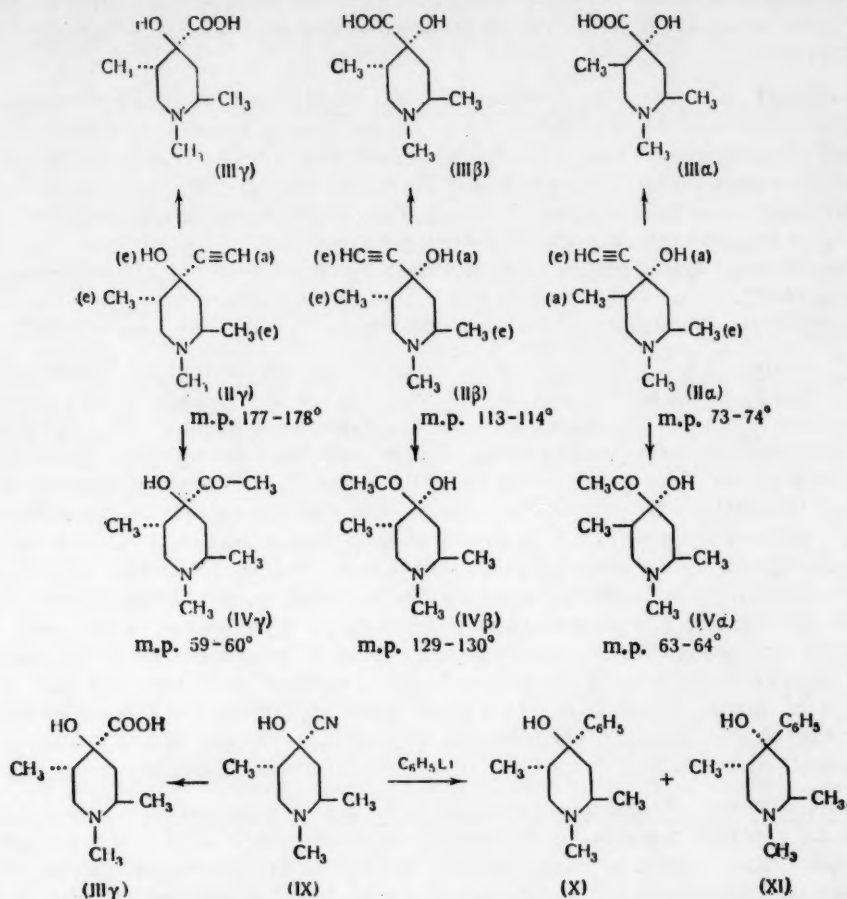
If these configurations are right, they must relate also to the corresponding isomeric acetylenic alcohols (II α , β , γ), since their hydrogenation to the corresponding 1, 2, 5-trimethyl-4-ethyl-4-piperidinols (I α , β , γ) does not affect the asymmetry centers. With the trans-arrangement of methyl groups acetylenic alcohol (II β) will have the ethynyl group in the trans-position relative to the methyl group on C₅, whereas in its C₄ epimer (II γ) these groups will have the cis-arrangement. According to this the ethynyl group in the isomeric acetylenic alcohol (II α) should occupy the cis-position relative to the cis-methyl groups on C₂ and C₅.

The conversions of isomeric acetylenic alcohols (II α , β , γ) to the corresponding hydroxy acids (III) and ketols (IV), which were carried out earlier [4], show that these last must have steric structures corresponding to the original acetylenic alcohols.

Certain chemical conversions of isomeric acetylenic alcohols (II α , β , γ), hydroxy acids (III α , β , γ), and ketols (IV α , β , γ), which we studied, enabled us to obtain some additional confirmations of the correctness of the configurations adopted for them. If the steric structure of every isomer prepared is actually correct, β -series compounds in their stable conformation must have the hydroxyl group in the axial position whereas the epimeric γ -series compounds will have this group in the equatorial position. According to this, these two series of compounds will differ from one another in dehydration and esterification reactions; this was observed experimentally. It was found that the β -series hydroxy ester and ketol (III β) (corresponding to the number of the hydroxy acid) and (IV β) give individual crystalline dehydration products in good yield on treatment with hydrogen chloride in alcoholic solution even at room temperature, which may indicate the presence of axial hydroxyl groups in them. The hydroxy ester α -isomer (III α) also proved easy to dehydrate. Contrary to this, the γ -series hydroxy ester and ketol (III γ) and (IV γ) are unable to split out water under similar conditions, which may in some measure indicate that their hydroxyl groups lie in the equatorial position.

As was shown earlier [6], acetylenic alcohols of the β -series are much more difficult to esterify at the hydroxyl group than the corresponding γ -series compounds, and this also may serve as confirmation of the presence of axial hydroxyl in acetylenic alcohols of the (III γ) type. The facts, observed earlier [4], of the easier oxidation of the acetylenic alcohol γ -isomer (II γ) and its more difficult hydration to the ketol (IV γ) also correspond to the configurations of acetylenic alcohols, adopted by us.

All the results considered, enable us to express certain views on the configuration of cyanhydrin (IX), obtained as the only product of the reactions of 1, 2, 5-trimethyl-4-piperidone with hydrogen cyanide [7] and acetone cyanhydrin [8].



Since it was found that its hydrolysis gives only the hydroxy acid γ -isomer (III γ), whereas the reaction with phenyllithium leads to a mixture of the earlier-described 1, 2, 5-trimethyl-4-phenyl-4-piperidinol γ - (X) and β - (XI) isomers [2, 9], cyanhydrin (IX) quite probably has the configuration corresponding to the trans-arrangement of the cyano group relative to the methyl group on C₂. The hypothesis of the contrary configuration of this cyanhydrin, advanced earlier [7], is hereby amended.

EXPERIMENTAL

Hydrogenation of Isomeric Acetylenic Alcohols (II α , β , γ). A solution of 10 g of 1, 2, 5-trimethyl-4-ethynyl-4-piperidinol α -isomer (II α), m.p. 73-74° [4], in 100 ml of anhydrous alcohol was hydrogenated over Raney nickel. After absorption of 2 moles of hydrogen the alcohol was driven off and the oily residue distilled in vacuo. There was obtained 8.3 g of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol α -isomer (I α) in the form of a colorless, mobile liquid with b.p. 72-73° (3 mm). Found: N 8.26, 7.93%. C₁₀H₂₁ON. Calculated: N 8.18%. The methiodide of this isomer had m.p. 125-126° (from alcohol). Found: N 4.71, 4.80%. C₁₁H₂₄ONJ. Calculated: N 4.47%.

A solution of 10 g of 1, 2, 5-trimethyl-4-ethynyl-4-piperidinol β -isomer (II β), m.p. 113-114° [3], in 100 ml of anhydrous alcohol was hydrogenated over Raney nickel. A 3045-ml volume of hydrogen (20°, 750 mm) was absorbed, as compared to 2900 ml required by theory. The catalyst was filtered out and the alcohol distilled off in vacuo. After recrystallization of the solid residue from petroleum ether there was obtained 9.3 g of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol β -isomer (I β), m.p. 87-88°, identical with that described earlier [3]. The methiodide of this isomer had m.p. 259-260° (from alcohol). Found: N 4.34, 4.32%. C₁₁H₂₄ONJ. Calculated: N 4.47%.

A solution of 10 g of 1, 2, 5-trimethyl-4-ethynyl-4-piperidinol γ -isomer (II γ), m.p. 177-178° [3], in 150 ml of methanol was hydrogenated over Raney nickel. After absorption of 2 moles of hydrogen the catalyst was filtered out, the methanol distilled off, and the residue crystallized from acetone; there was obtained 8.9 g of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol γ -isomer (I γ), m.p. 80-81°, identical with that described earlier [3]. The methiodide, obtained by the usual method, had m.p. 173-174° (from anhydrous alcohol). Found: N 4.24, 4.42%. $C_{11}H_{24}ONJ$. Calculated: N 4.47%.

Reaction of trans-1, 2, 5-Trimethyl-4-piperidone (V) with Ethyllithium. To the ethyllithium solution prepared from 54 g of ethyl bromide and 7.5 g of lithium in 150 ml of ether, 33 g of trans-1, 2, 5-trimethyl-4-piperidone (V) was added during 15 min, the mixture being cooled with ice and stirred; stirring was continued for 1 hour more at 20°, after which the reaction mass was decomposed by adding 200 ml of water. The ether layer was separated and dried, the ether driven off, and the residue fractionated in vacuo. Ten g of the original 1, 2, 5-trimethyl-4-piperidone was recovered, and 7 g of a mixture of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol γ - and β -isomers, b.p. 100-105° (5 mm), was obtained. On addition of 5 ml of heptane to this mixture 5.5 g of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol γ -isomer (I γ), m.p. 79-80°, was isolated. On addition of 2 ml of methyl iodide to the mother liquor there was obtained 1.2 g of the methiodide of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol β -isomer (I β), m.p. 257-258°.

Reaction of a Mixture of 1, 2, 5-Trimethyl-4-piperidone Isomers with Ethyllithium. To the ethyllithium solution prepared from 18.3 g of ethyl bromide and 2.5 g of lithium in 100 ml of ether, 9.5 g of a mixture of 1, 2, 5-trimethyl-4-piperidones (V) and (VI), in which the cis-isomer (VI) predominated (m.p. -30 to -50°), was added during 15 min. The reaction mass was decomposed by adding 20 ml of water, the ether layer separated, and the reaction product fractionated in vacuo. There were obtained 4 g of the original 1, 2, 5-trimethyl-4-piperidone and 5 g of a mixture of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol isomers, from which, on addition of 5 ml of heptane, 1 g of the γ -isomer (I γ) separated out; m.p. 79-80°. A mixture of the γ - and β -isomers of (II) separated out from the mother liquor on cooling with dry ice (about 0.3 g of product m.p. 50-70°). On addition of 0.5 ml of methyl iodide to this mixture, a mixture of the methiodides of (I β) and (I γ) was obtained; on recrystallization of the latter from alcohol, 0.1 g of methiodide of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol β -isomer (I β) was isolated. After removal of the γ -isomer (I γ) and the crystalline mixture of β - and γ -isomers the mother liquor was fractionated in vacuo; the oil obtained (1.2 g) was cooled with dry ice; the crystals which separated were filtered out, and 1 ml of methyl iodide was added to the filtrate. As a result of several recrystallizations of the resulting precipitate from an alcohol-ether mixture and from alcohol, there were obtained about 0.1 g of the methiodide of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol α -isomer (I α), m.p. 124-126°, and 1.5 g of a mixture of isomeric methiodides, with m.p. 120-150°.

1, 2, 5-Trimethyl-4-ethyl- Δ^5 -dehydro-4-piperidinol (VIII) and its Hydrogenation. To the ethyllithium solution prepared from 2.5 g of lithium and 18.3 g of ethyl bromide in 100 ml of ether, 6 g of 1, 2, 5-trimethyl- Δ^5 -dehydro-4-piperidone (VII) was added, the mixture being cooled with ice [1]; the reaction mass was stirred for 2 hrs at room temperature and decomposed with water (50 ml). The ether layer was separated, the ether driven off, and the residue fractionated in vacuo. There were obtained 1.3 g of a fraction with b.p. 90-100° (3 mm) and 2 g of a fraction with b.p. 110-120° (4 mm). On addition of 3 ml of isooctane to the latter and cooling with dry ice, 1.2 g of 1, 2, 5-trimethyl-4-ethyl- Δ^5 -dehydro-4-piperidinol (VIII), m.p. 40-41°, was isolated. Found: C 70.72, 70.99; H 11.24, 11.37%. $C_{10}H_{19}ON$. Calculated: C 71.00; H 11.25%.

A solution of 1 g of 1, 2, 5-trimethyl-4-ethyl- Δ^5 -dehydro-4-piperidinol (VIII) in 25 ml of methanol was hydrogenated for 6 hr over Raney nickel; during this time 150 ml of hydrogen was absorbed. Then the catalyst was filtered out, the methanol distilled off, and the residue fractionated in vacuo. There was obtained about 0.5 g of an oil with b.p. 90-100° (5 mm), to which 10 ml of ether and 1 ml of methyl iodide were added. The mixture of isomeric methiodides, which precipitated, was recrystallized from 5 ml of alcohol, and the prismatic crystals of the methiodide of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol α -isomer (I α) were selected, and recrystallized from acetone. Thus there was obtained about 0.1 g of the methiodide of the α -isomer (I α), m.p. 124-125°, which gave no depression with a known sample. The crystalline methiodide mixture, remaining after removal of the α -isomer, was recrystallized twice from an alcohol-ether mixture. There was obtained 0.1 g of the methiodide of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol β -isomer (I β), m.p. 255-256°.

Dehydration of 1, 2, 5-Trimethyl-4-carbomethoxy-4-piperidinol Isomers (III α , β , γ). A solution of 0.7 g of 1, 2, 5-trimethyl-4-carbomethoxy-4-piperidinol α -isomer (III α), m.p. 77-78° [4], in 40 ml of anhydrous alcohol was saturated with dry hydrogen chloride and left for 12 days at room temperature. After removing the alcohol the solid residue was recrystallized from an acetone-alcohol mixture. There was obtained 0.5 g of the hydrochloride of the dehydration product, m.p. 184.5-186°. Found: N 5.91, 6.08%. $C_{10}H_{18}O_2NCl$. Calculated: N 6.35%.

A solution of 3 g of 1, 2, 5-trimethyl-4-carbomethoxy-4-piperidinol β -isomer (III β), m.p. 70-71° [4], in 30 ml of anhydrous alcohol was saturated with dry hydrogen chloride and left for 12 days at room temperature. After treatment as indicated above, 2.5 g of the hydrochloride of the dehydration product, m.p. 155-156° (from acetone), was obtained. Found: N 6.34, 6.26. $C_{10}H_{18}O_2NCl$. Calculated: N 6.35%.

Under similar conditions 3 g of 1, 2, 5-trimethyl-4-carbomethoxy-4-piperidinol γ -isomer (III γ), m.p. 117-118° [4], gave 2.5 g of the hydrochloride of the original hydroxy ester (III γ), m.p. 125-126° (from alcohol), which proved to be identical with a known prepared sample. Found: N 6.15, 5.78%. $C_{10}H_{20}O_3NCl$. Calculated: N 5.90%.

Hydration of 1, 2, 5-Trimethyl-4-ethynyl-4-piperidinol Isomers (II β , γ). To a solution of 2 g of mercuric sulfate and 4 ml of concentrated sulfuric acid (sp. gr. 1.84) in 40 ml of water, 5 g of 1, 2, 5-trimethyl-4-ethynyl-4-piperidinol γ -isomer (II γ), m.p. 177-178° [3], was gradually added. After addition of the acetylenic alcohol, stirring was continued for 3 hours in a boiling water bath. The solution was neutralized with potash, treated with zinc dust, saturated with potash, and extracted with ether. After removing the ether there was obtained 4.9 g of ketoalcohol (IV γ), m.p. 59-60° (from gasoline) [10].

In the case of 1, 2, 5-trimethyl-4-ethynyl-4-piperidinol β -isomer (II β), m.p. 113-114°, the same quantities of starting materials, with stirring for 1 hour at room temperature and subsequent treatment of the reaction product as described above, gave 4.1 g of the ketoalcohol β -isomer (IV β), m.p. 129-130° [10]. The reaction was exothermic, and the reaction mixture warmed up to 35-40°.

Dehydration of 1, 2, 5-Trimethyl-4-acetyl-4-piperidinol Isomers (IV β , γ). A solution of 4 g of 1, 2, 5-trimethyl-4-acetyl-4-piperidinol β -isomer (IV β), m.p. 129-130° [10], in 40 ml of anhydrous alcohol was saturated with dry hydrogen chloride. After the usual treatment there was obtained 2.2 g of the hydrochloride of the dehydration product, m.p. 148-149°. Found: N 6.53, 6.72%. $C_{10}H_{18}ONCl$. Calculated: N 6.85%.

Under similar conditions 4 g of 1, 2, 5-trimethyl-4-acetyl-4-piperidinol γ -isomer (IV γ), m.p. 59-60°, gave 3 g of the hydrochloride of the original ketol (IV γ), m.p. 181-183° (from alcohol), which proved to be identical with a sample prepared from ketol (IV γ) in the usual way. Found: N 6.18, 6.36%. $C_{10}H_{20}O_2NCl$. Calculated: N 6.29%.

Reaction of 1, 2, 5-Trimethyl-4-piperidone Cyanhydrin (IX) with Phenyllithium. A 33.6 g quantity of 1, 2, 5-trimethyl-4-piperidone cyanhydrin [7] was added to the phenyllithium solution prepared from 58 g of bromobenzene and 5.6 g of lithium. After the usual treatment there was obtained 31 g of a mixture of 1, 2, 5-trimethyl-4-phenyl-4-piperidinol isomers, which on recrystallization from isooctane gave 12 g of 1, 2, 5-trimethyl-4-phenyl-4-piperidinol γ -isomer (X), m.p. 106-107° [2, 9]. On addition of 10 ml of saturated alcoholic hydrogen chloride solution to the mother liquor 8.2 g of the hydrochloride of 1, 2, 5-trimethyl-4-phenyl-4-piperidinol β -isomer (XI) [2, 9] was obtained. The uncrystallized part of the hydrochloride was converted to a mixture of bases, from which 4.3 g of alcohol (X) was isolated.

SUMMARY

On the basis of a number of chemical reactions, views are expressed on the possible steric structure of 1, 2, 5-trimethyl-4-ethyl-4-piperidinol isomers (I α , β , γ), the corresponding acetylenic alcohols (II α , β , γ), and certain piperidine derivatives obtained from them.

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CHEMISTRY OF DIHYDRORESORCINOL

ARTICLE 7. INTERACTION OF CYCLIC β -DICARBONYL COMPOUNDS WITH HYDROGEN PEROXIDE IN AN ALKALINE MEDIUM

S. I. Zav'yalov, A. F. Vasil'ev, and L. P. Vinogradova

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

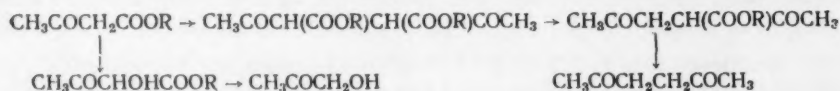
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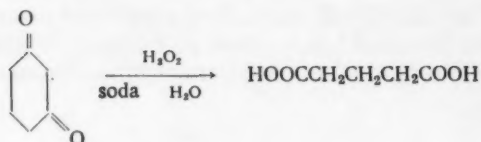
pp. 849-853, May, 1961

Original article submitted May 3, 1960

It is well known [1] that the oxidation of acetoacetic ester by hydrogen peroxide in an alkaline medium leads to a complex mixture consisting of acetonylacetone, carbethoxyacetonylacetone, hydroxyacetone, and other products. This reaction probably goes through intermediate stages of formation of α -hydroxyacetoacetic and bisacetoacetic esters, which undergo further conversions under the experimental conditions:



It was of interest to investigate the behavior of dihydroresorcinol and its derivatives toward alkaline hydrogen peroxide, since in many cases cyclic β -diketones substantially differ from aliphatic β -dicarbonyl compounds in their chemical properties. We found that dihydroresorcinol reacts violently with hydrogen peroxide in an alkaline medium to form glutaric acid which obviously is the result of oxidative cleavage of the dihydroresorcinol ring:



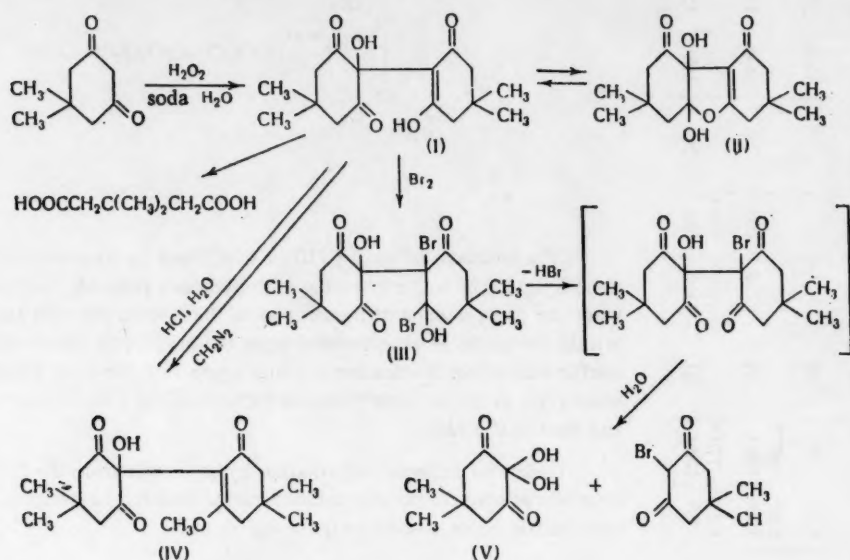
Oxidative cleavage of dihydroresorcinol cannot be avoided even by gradual addition of an equivalent of hydrogen peroxide at a temperature which is not allowed to rise above 15-20°.

A different behavior toward hydrogen peroxide is displayed by dimedon, which under these conditions forms not only β , β -dimethylglutaric acid, but also a substance of composition $\text{C}_{16}\text{H}_{22}\text{O}_5$. On the basis of its chemical and physicochemical properties the reaction product of dimedon and hydrogen peroxide may be assigned the structure of the tricyclic diol form of 2-hydroxybisdimedon (II).

Diol (II) titrates as a monobasic acid and reacts with excess diazomethane to give monomethyl ether (IV), which on treatment with dilute hydrochloric acid is easily hydrolyzed to the original diol (II). The oxidation of diol (II) by hypobromite in an alkaline medium leads to β , β -dimethylglutaric acid. The bromination of diol (II) in chloroform gives dibromide (III), which loses hydrogen bromide on heating with soda solution, and gives a mixture of 2-bromodimedon and an oily substance which probably is 5, 5-dimethylcyclohexanetrione-1, 2, 3 hydrate (V) or a conversion product thereof. The ease of hydrolytic cleavage of dibromide (III) is due to the presence of a hydroxy-ketonic grouping in its molecule [2].

Diol (II) has three bands in the 1500-1800 cm^{-1} region, which may be referred to valence vibrations of the non-conjugated keto group (1712 cm^{-1}), the conjugated keto group (1647 cm^{-1}), and the double bond conjugated with the

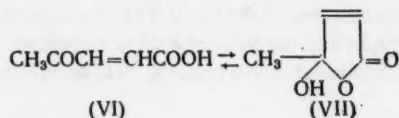
keto group (1612 cm^{-1}) (table). If the triketoenol structure (I) is adopted for the reaction product of dimedon and hydrogen peroxide, the absence of the two carbonyl bands characteristic of β -dicarbonyl compounds might be explained by the presence of a hydrogen bond causing weakening of the β -keto-group interaction and merging of the two frequencies into a single band (1712 cm^{-1}). The half-width of this band (30 cm^{-1}) actually is somewhat greater than that of the band (1695 cm^{-1}) of methyl ether (IV) which, as follows from the IR spectrum, has the triketoenol



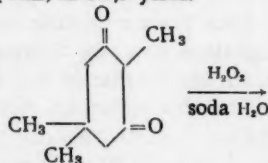
structure. But the absorption coefficient (K) of the triketoenol (I) would be about twice as great as the corresponding coefficient of methyl ether (IV); in fact, this is not observed.

In the spectrum of diol (II) there is only one frequency of the OH valence vibration, and its absorption coefficient is twice as great as for methyl ether (IV); this indicates the presence of two hydroxyl groups of the same kind in the diol (II) molecule. Diol (II) exists only in the enol form, since its spectra do not show the changes characteristic of keto-enol tautomeric equilibrium either in the crystalline state or in chloroform at a very low concentration. In the ultraviolet region diol (II)* and its methyl ether (IV) have maxima at $263\text{ m}\mu$ ($\epsilon\ 10850$) and $265\text{ m}\mu$ ($\epsilon\ 12600$), respectively, practically coinciding with the maximum of 2-methyldimedon ($264\text{ m}\mu$) (alcoholic solutions).

Thus the reaction product of dimedon and hydrogen peroxide has the diol form (II) both in the crystalline state and in chloroform; however, it can react also in the triketoenol form (I), e.g., in the formation of methyl ether (IV) on treatment with diazomethane. A similar phenomenon is noted in the case of β -acetylacrylic acid (VI) and its derivatives, which exist in the hydroxylactone form (VII) [2]:

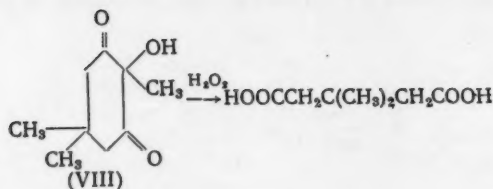


On treatment of 2-methyldimedon with hydrogen peroxide in an alkaline medium hydroxylation occurs, leading to the formation of 2-hydroxy-2-methyldimedon (VIII) in 52% yield:



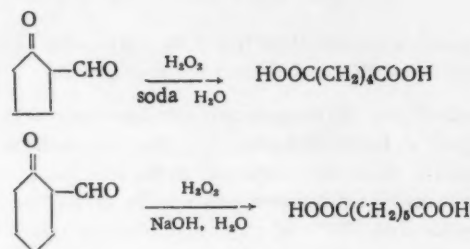
* The UV spectra were taken by V. M. Medvedeva.

Substance	Band 1			Band 2			Band 3			Band 4			Band 5		
	ν , cm^{-1}	K	$\frac{1}{\Delta\nu}, \text{cm}^{-1}$	ν , cm^{-1}	K	$\frac{1}{\Delta\nu}, \text{cm}^{-1}$	ν , cm^{-1}	K	$\frac{1}{\Delta\nu}, \text{cm}^{-1}$	ν , cm^{-1}	K	$\frac{1}{\Delta\nu}, \text{cm}^{-1}$	ν , cm^{-1}	K	$\frac{1}{\Delta\nu}, \text{cm}^{-1}$
II in CHCl_3	1612	1240	23	1647	1015	20	1712	980	30				3438	230	120
II, crystalline film in vaseline	1616	1000*		1646	900*		1692	940*					3448	110	115
IV in CHCl_3	1598	1282	20	1647	715	16	1695	1245	24						
IV, crystalline film in vaseline	1597	1000*		1641	605*		1700	770*					3486	127	110
VIII in CHCl_3							1696	1580	27						



The structure of ketol (VIII) is confirmed by its oxidation to β, β -dimethylglutaric acid on heating with hydrogen peroxide, and also the IR spectrum (the presence of frequencies of the β -diketone and alcohol groups). Within the limits of experimental error the arithmetic means of the absorption coefficients of the β -dicarbonyl bands agree well for ketol (VIII) and methyl ether (IV), as do the absorption coefficients of the OH valence-vibration bands and their half-widths.

Under the influence of alkaline hydrogen peroxide the 2-formyl derivatives of cyclopentanone and cyclohexanone undergo oxidative cleavage, adipic and pimelic acids, respectively, being formed:



EXPERIMENTAL

The spectra of the substances investigated were taken in an IKS-12 instrument with sodium chloride and lithium fluoride prisms, in standard separable cuvetts with a layer thickness from 0.05 to 0.5 mm, in chloroform at concentrations from 0.02M to 0.2 M. Substances in the crystalline state were spectrographed in the form of a 20 % suspension in Vaseline in a cuvet with a layer thickness of 0.008 mm. K was determined from the formula

$$K_v = \frac{\ln \frac{I_0}{I}}{cl},$$

where c is the concentration in moles/liter, and l is the layer thickness in mm. Since it was impossible to calculate light scattering on taking spectra in the crystalline state, the absorption coefficients in this case are relative in character, and are marked with asterisks in the table. The calculated spectral slit width with a sodium chloride prism is 8.1 cm^{-1} in the 1600 cm^{-1} region and 9.6 cm^{-1} in the 1700 cm^{-1} region; with a lithium fluoride prism it is 6.6 cm^{-1} in the 3500 cm^{-1} region.

Reaction of Dihydroresorcinol with Hydrogen Peroxide. To a solution of 2 g of dihydroresorcinol and 2.5 g of soda in 20 ml of water at 20-25°, 12 ml of 30% hydrogen peroxide was added during 20 min. After acidification with dilute hydrochloric acid, 1.3 g (54%) of glutaric acid, m.p. 95-96°, was extracted with ether.

Reaction of Dimedon with Hydrogen Peroxide. To a solution of 2.8 g (0.02 mole) of dimedon and 2 g of soda in 25 ml of water at 20-27°, 12 ml (0.1 mole) of 30% hydrogen peroxide was added during 30 min; after 20 min more the mixture was acidified with hydrochloric acid and the precipitated diol (II) recrystallized from aqueous methanol. Yield 2.2 g (75%); m.p. 138-139°. Found: C 65.21, 65.12; H 7.37, 7.51%. $C_{16}H_{22}O_5$. Calculated: C 65.29; H 7.53%. Determined titration equivalent 288, 290. $C_{16}H_{22}O_5$. Calculated titration equivalent 294.

On treatment with an excess of diazomethane in ether, diol (II) gave a nearly-quantitative yield of methyl ether (IV); m.p. 177-178° (from benzene). Found: C 66.54, 66.56; H 7.85, 7.95%. $C_{17}H_{24}O_5$. Calculated: C 66.21; H 7.85%.

On heating with dilute (1:1) hydrochloric acid (10-15 min, 60-70°), methyl ether (IV) was hydrolyzed to the original diol (II).

Bromination of Diol (II). To 2 g (0.007 mole) of diol (II) in 15 ml of dry chloroform at 10-15°, 2.5 g (0.015 mole) of bromine in 10 ml of dry chloroform was added. The resulting yellow precipitate was filtered out, and washed with chloroform. Two g of dibromide (III), m.p. 101-102° (decomp.), was obtained. Found: Br 32.61, 32.69%. $C_{16}H_{22}O_5Br_2$. Calculated: Br 33.0%.

Hydrolytic Cleavage of Dibromide (III). A mixture of 0.4 g of dibromide (III) and 0.1 g of soda in 5 ml of water was heated for 10 min at 50-60°. On acidification 0.08 g of 2-bromodimedon, m.p. 185-186°, was precipitated. About 0.02 g of an oil, giving a dark coloration with ferric chloride, was extracted from the aqueous mother liquor with ether.

Reaction of 2-Methyldimedon with Hydrogen Peroxide. To a mixture of 2 g (0.013 mole) of 2-methyldimedon and 1.5 g of soda in 15 ml of water and 15 ml of chloroform at 20-25° (vigorous stirring), 8 ml (0.07 mole) of 30% hydrogen peroxide was added during 10 min. From the chloroform layer there was isolated 1.2 g (52%) of 2-hydroxy-2-methyl-dimedon (VIII), m.p. 101-102° (from a benzene-heptane mixture). Found: C 63.51, 63.46; H 8.10, 8.21%. $C_9H_{14}O_3$. Calculated: C 63.51; H 8.29%.

When the reaction was carried out in the absence of chloroform the yield of 2-hydroxy-2-methyldimedon was decreased owing to the formation of β , β -dimethylglutaric acid.

Reaction of 2-Formylcyclopentanone with Hydrogen Peroxide. To a mixture of 2.9 g of 2-formylcyclopentanone and 2.6 g of soda in 26 ml of water at 15-22°, 15 ml of 30% hydrogen peroxide was added during 20 min. The resulting solution was extracted with ether to remove neutral impurities, and then was acidified with dilute hydrochloric acid; 3.6 g (98%) of adipic acid, m.p. 149-151°, was extracted with ether.

Reaction of 2-Formylcyclohexanone with Hydrogen Peroxide. To a mixture of 3.6 g of 2-formylcyclohexanone and 1.4 g of sodium hydroxide in 14 ml of water at 18-25°, 13 ml of 30% hydrogen peroxide was added during 30 min. After the treatment described above, 2.3 g (40%) of pimelic acid, m.p. 98-100°, was obtained. Cyclohexanone was isolated from the neutral fraction, in the form of the 2, 4-dinitro-phenylhydrazone (m.p. 160-162°).

SUMMARY

1. On treatment with alkaline hydrogen peroxide, dihydroresorcinol and the 2-formyl derivatives of cyclopentanone and cyclohexanone undergo oxidative cleavage, glutaric, adipic, and pimelic acids, respectively, being formed. Under these conditions dimedon is converted to the diol form of 2-hydroxybisdimedon.
2. In the reaction of 2-methyldimedon with hydrogen peroxide in an alkaline medium, hydroxylation takes place and the corresponding hydroxy derivative is obtained.

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HYDRODEALKYLATION OF HOMOLOGS OF CYCLOHEXANE OVER NICKEL/ALUMINA CATALYST UNDER HYDROGEN PRESSURE

N. I. Shuikin and T'ien Hsing-hua

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR
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In the preceding investigation [1], devoted to the hydrodemethylation of methylcyclohexane over nickel catalysts in a flow system under pressure, we established the conditions for obtaining up to 30% yield of cyclohexane, calculated on the converted methylcyclohexane. At the same time dehydrogenation of the initial methylcyclohexane and of the resulting cyclohexane were reduced to a minimum, and the yield of toluene and benzene did not exceed 17%. It was therefore of interest to clarify the possibility of dealkylation under the same conditions of other related monosubstituted homologs of cyclohexane, namely ethyl-, n-propyl-, and isopropylcyclohexanes, in presence of 10% nickel/alumina catalyst. The latter had manifested the maximum activity and specificity in the demethylation of methylcyclohexane [1]. One of us had made some observations along these lines in the examination of the catalytic transformations of ethylcyclohexane over $\text{Pd} - \text{Al}_2\text{O}_3$ [2].

According to the literature [3, 4] the dehydrogenation of ethylcyclohexane, n-butylcyclohexane, and tert-butylcyclohexane at normal pressure over $\text{Ni} - \text{Al}_2\text{O}_3$ catalyst at 350° is accompanied by considerable hydrocracking of the side chains and by predominant formation of toluene. Hydrogen pressure can be expected to retard the dehydrogenation of the hexamethylene ring and so enable the course of hydrogenolysis of the side chain to be more clearly followed.

Our experimental results are of fundamental interest from the aspect of evaluation of the relative strength of C - C bonds in molecules of alkylcyclohexanes. They show that the bond between a ring carbon atom and the nearest side chain carbon is stronger than the C - C bond in the substituent. The energy of rupture of the C - C bond between the methyl group and the benzene ring in toluene ($C_{\text{arom}} - C_{\text{aliph}})$ is estimated at about 91 kcal, while that of the $C_{\text{aliph}} - C_{\text{aliph}}$ bond (in ethane and propane) is 82-83 kcal [5]. The energy of rupture of the $C_{\text{alicyc}} - C_{\text{aliph}}$ bond will obviously be intermediate in value, as our work has confirmed. These considerations provide an explanation of the predominant formation of methylcyclohexane, and not of cyclohexane or ethylcyclohexane, during hydrogenolysis of substituents in the molecules of n-propyl- and isopropylcyclohexanes.

EXPERIMENTAL

The initial hydrocarbons had the following characteristics:

B.p. $^\circ\text{C}$	(760 mm)	n_D^{20}	d_4^{20}
Ethylcyclohexane	131.4	1.4331	0.7880
n-Propylcyclohexane	156.7	1.4370	0.7941
Isopropylcyclohexane	154.5	1.4410	0.8025

The experimental study of the transformations of these hydrocarbons was carried out with a flow apparatus [6] at 360° and 20 atm in presence of 10% $\text{Ni} - \text{Al}_2\text{O}_3$ catalyst [1]. The hydrocarbons were passed through at a space velocity of 0.2 hr^{-1} with a 4:1 molar ratio of hydrogen to hydrocarbon. The catalyzates (yields 78-80%) were resolved by chromatography on silica gel into paraffinic-naphthenic and aromatic portions. Results of fractionation of the paraffinic-naphthenic portion in a 40-plate column are set forth in Tables 1-3.

TABLE 1. Fractionation and Properties of Paraffinic - Naphthenic Part of Ethylcyclohexane Catalyzate

Fraction	Boiling range in °C (760 mm)	Yield in weight-% of catalyzate	Properties	
			n_D^{20}	d_4^{20}
I	40,0—80,0	4,4	1,4090	0,7298
II*	80,0—81,5	4,8	1,4258	0,7780
III	81,5—100,0	5,6	1,4180	0,7576
IV*	100,0—101,0	33,3	1,4231	0,7688
V	101,0—130,7	6,6	1,4231	0,7683
VI*	130,7—131,7	16,6	1,4335	0,7876
Residue	—	5,1	—	—

* Fractions II, IV, and VI consisted mainly of cyclohexane, methylcyclohexane, and ethylcyclohexane respectively.

TABLE 2. Fractionation and Properties of Paraffinic - Naphthenic Portion of n-Propylcyclohexane Catalyzate

Fraction	Boiling range in °C (760 mm)	Yield in wt. % of catal.	Properties	
			n_D^{20}	d_4^{20}
I	40,0—79,8	4,8	1,3970	0,7075
II*	79,8—81,3	5,9	1,4260	0,7778
III	81,3—99,3	7,1	1,4132	0,7486
IV*	99,3—100,9	20,3	1,4231	0,7694
V	100,9—131,0	6,7	1,4200	0,7592
VI*	131,0—132,5	3,0	1,4325	0,7873
VII	132,5—155,8	5,1	1,4310	0,7820
VIII**	155,8—156,4	16,4	1,4376	0,7940
Residue	—	2,8	—	—

* Fractions II, IV, and VI mainly consist of cyclohexane, methylcyclohexane, and ethylcyclohexane respectively.

** The properties of fraction VIII are the same as those of n-propylcyclohexane.

TABLE 3. Fractionation and Properties of Paraffinic - Naphthenic Portion of Isopropylcyclohexane Catalyzate

Fraction	Boiling range in °C (760 mm)	Yield in wt. % of catal.	Properties	
			n_D^{20}	d_4^{20}
I	52,0—80,0	3,0	1,4010	0,7150
II*	80,5—81,5	5,2	1,4250	0,7776
III	81,5—100,0	3,6	1,4160	0,7488
IV*	100,0—101,5	20,2	1,4230	0,7688
V	101,5—131,0	4,8	1,4220	0,7547
VI*	131,0—132,0	12,5	1,4330	0,7882
VII	132,0—154,3	4,1	1,4335	0,7890
VIII**	154,3—155,0	12,6	1,4400	0,8025
Residue	—	2,9	—	—

* Fractions II, IV, and VI consist mainly of cyclohexane, methylcyclohexane, and ethylcyclohexane respectively.

** Fraction VIII consists mainly of the initial isopropylcyclohexane.

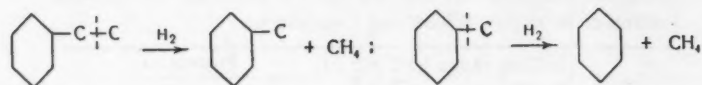
The aromatic portion of the catalyzate was also fractionated in a column and subjected to spectroscopic examination. Xylenes and other disubstituted alkylbenzenes were not detected. The escaping gases were analyzed by gas chromatography. Data for the aromatic portion and the released gases are set forth in Table 4.

TABLE 4. Composition of Aromatic Portion of Catalyzate and of the Gaseous Products

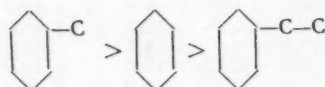
Composition of aromatic hydrocarbons and gaseous products, %	Initial hydrocarbons		
	Ethylcyclohexane	n-Propylcyclohexane	Isopropylcyclohexane
Aromatic portion			
Benzene	1.2	0.7	1.7
Toluene	10.5	9.7	10.8
Ethylbenzene	8.4	2.4	7.6
n-Propylbenzene	—	10.9	—
Isopropylbenzene	—	—	5.9
Gas evolved, vol.-%			
H ₂	89.5	79.4	84.3
CH ₄	10.1	18.2	15.3
C ₂ H ₆	0.1	2.1	—
C ₃ H ₈	—	0.3	—
C ₂ H ₄	Traces	—	0.4

The results show that under the present conditions ethylcyclohexane, n-propyl-, and isopropylcyclohexane are not only subjected to hydrogenolysis of the side chains but also undergo dehydrogenation to the corresponding aromatic hydrocarbons. Products of dealkylation of the initial cyclanes also undergo dehydrogenation. To a very slight extent the six-membered cyclanes also undergo isomerization with ring contraction to give the corresponding five-membered hydrocarbons which then undergo hydrogenolysis in the ring with formation of alkanes.

Under identical conditions the degree of conversion and the extent of hydrogenolysis of the side chain of the alkylcyclanes are greater than in the case of methylcyclohexane. In each case the yield of methylcyclohexane is greater than that of the other cyclanes. This points to the C—C bond between the methyl group and the hexamethylene ring being stronger than the other C—C bonds of the side chains. The data of Tables 1 to 4 indicate that ethylcyclohexane undergoes demethylation in a series of steps because the ethane content of the gases is extremely low.

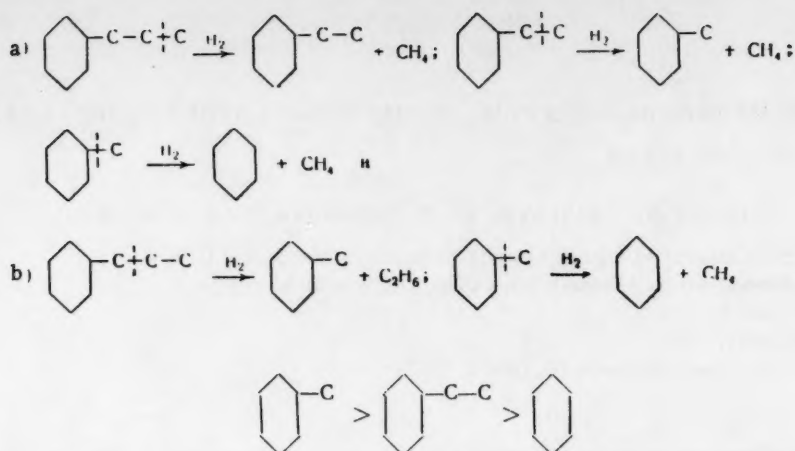


We see from the data of Table 2 that in hydrogenolysis of the side chain of n-propylcyclohexane the yields of cyclohexane, methylcyclohexane, and ethylcyclohexane decrease in the following sequence:



On the basis of these facts and of the analysis of the gases (see Table 4) we may suggest that hydrogenolysis of the side chain of n-propylcyclohexane follows two routes: a) Stepwise demethylation; b) detachment of the ethyl group with formation of methylcyclohexane. Comparison of the results of hydrogenolysis of ethyl- and n-propylcyclohexane leads to the conclusion that rupture of the C—C bonds in the side chain takes place more easily than that of the bond between the ring carbon atom and the nearest atom of the side chain.

We see from the data of Table 3 that the yields of products of hydrogenolysis of isopropylcyclohexane decrease in a sequence different from that in the case of n-propylcyclohexane:



A possible explanation is that the ethyl group cannot split off during hydrogenolysis of isopropylcyclohexane, whereas the probability of detachment of a methyl group is greater in this case than in that of n-propylcyclohexane.

The authors thank R. N. Shafran for analyzing the gaseous products.

SUMMARY

1. A study was made of the hydrogenolysis of the side groups of ethylcyclohexane, n-propyl-, and isopropylcyclohexanes in presence of 10% Ni-Al₂O₃ catalyst at a hydrogen pressure of 20 atm and 360° in a flow system.
2. The main product of hydrogenolysis of these alkylcyclohexanes in all cases is methylcyclohexane.
3. The preferential formation of methylcyclohexane indicates that the bond between a ring carbon and an adjacent carbon atom of a side chain is stronger than the C-C bonds of the aliphatic substituent.

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CATALYTIC DEHYDROCHLORINATION OF METHYLCHLOROCYCLOHEXANES TO METHYLCYCLOHEXENES

N. I. Shuikin, E. D. Tulupova, Z. P. Poyakova, and D. A. Kondrat'ev

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

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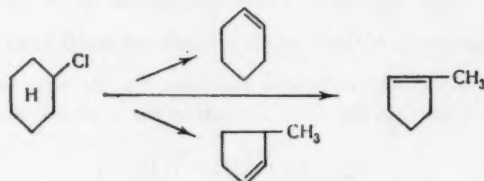
Nauk, 1961, No. 5,

pp. 858-863, May, 1961

Original article submitted March 16, 1960

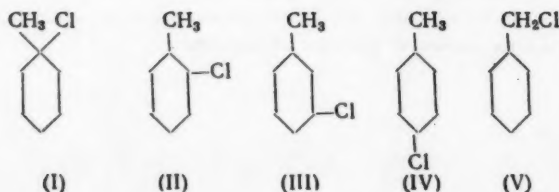
New methods of preparation of six-membered cyclenes are now not only of scientific but also of practical interest because they can serve as initial substances for synthesis of adipic and alkyladipic acids which in turn are monomers for production of synthetic resins and of valuable esters.

Several authors [1-3] have shown that cyclohexene can be obtained by catalytic cleavage of the elements of hydrogen chloride from the molecule of monochlorocyclohexane at elevated temperatures. One of us [4] showed earlier that at 300°, in presence of a mixed catalyst consisting of $Al_2O_3 + Fe_2O_3$, formation of cyclohexene from monochlorocyclohexane can be accompanied by isomerization of the six-membered ring to a five-membered ring by the following mechanism:

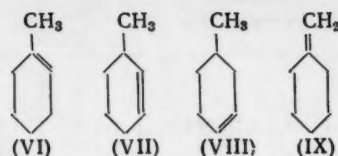


The monohalogenated hydrocarbons of the cyclohexane series used for this reaction can be prepared in high yields by photochlorination of the corresponding hydrocarbons with free chlorine. Certain regularities were established in studies of photochlorination of cyclohexane hydrocarbons by Russian [4-6] and foreign [7-10] workers. Increasing attention has been paid in recent years to the chlorination of C_5 to C_7 cyclanes [11-13] due to the application of chlorination of these hydrocarbons to the preparation of insecticides.

In the present work we carried out the synthesis of methylcyclohexenes by catalytic dehydrochlorination of monochloro derivatives of methylcyclohexane. Our investigation had the following objectives: 1) Establishment of the optimum conditions for the photochlorination of methylcyclohexane; 2) study of the conditions for smooth dehydrochlorination of a mixture of methylchlorocyclohexanes obtained by chlorination of methylcyclohexane and also synthesized by us from the corresponding individual methylcyclohexanols; 3) determination of the structure of the methylcyclohexenes obtained by catalytic dehydrochlorination. Formation of the following four isomeric methylchlorocyclohexanes (I-IV) and of chloromethylcyclohexane (V) is theoretically possible in the photochlorination of methylcyclohexane:



Consequently the dehydrochlorination of this mixture of monochloro derivatives or of methylcyclohexane may be expected to lead to three isomeric methylcyclohexenes (VI-VIII) and methylenecyclohexane (IX):



The investigation established that chlorination of methylcyclohexane in the liquid phase in diffuse daylight at room temperature in a static system gave products containing 79-81% methylchlorocyclohexanes, 9.7-12.7% methyl-dichlorocyclohexanes, and 2.2-3.3% methyltrichlorocyclohexanes, calculated on the reacted methylcyclohexane. Under these conditions the quantity of methylcyclohexane entering into reaction in one chlorination operation was 29.5-30%. Unreacted hydrocarbon was distilled from the reaction products and again subjected to chlorination.

Dehydrochlorination experiments were run at 220°, atmospheric pressure, and a space velocity of 1 hr⁻¹ in presence of activated birch carbon or barium chloride deposited in the proportion of 5% on active carbon. Under these conditions the elements of hydrogen chloride were split off smoothly from methylchlorocyclohexanes to give a mixture of methylcyclohexenes in a yield of 63 to 77.6%. Gas-liquid chromatographic analysis of the dry catalyzate (after purification from hydrogen chloride) revealed that the main products of dehydrochlorination of a mixture of methylchlorocyclohexanes are 1-methylcyclohexene-1 (24.5-42.0%) and 1-methylcyclohexene-3 (58.0-75.5%). On the basis of the analytical data for the resulting mixture of methylcyclohexenes, we may assume that the monochloro derivatives obtained in the photochlorination of methylcyclohexane comprise a mixture of the four isomeric methylchlorocyclohexanes (I) - (IV). These compounds are known to have very similar boiling points and other constants, so that their separation even by precision fractionation is impossible. It was established by the same method that dehydrochlorination of the product of interaction of 1-methylcyclohexanol-2 with concentrated hydrochloric acid gives all of the three isomeric methylcyclohexenes: 1-methylcyclohexene-1 (17.1%), 1-methylcyclohexene-2 (8.5%), and 1-methylcyclohexene-3 (71.3%). The presence of 1-methylcyclohexene-3 in the resulting mixture of methylcyclohexenes shows that reaction of 1-methylcyclohexanol-2 with hydrochloric acid gives not a single chloride (1-methyl-2-chlorocyclohexane) but a mixture of methylchlorocyclohexanes which lose the elements of hydrogen chloride to give a mixture of the three isomeric methylcyclohexenes. Formation of a mixture of isomeric methylchlorocyclohexanes on interaction of 1-methylcyclohexanol-2 with hydrochloric acid is also confirmed by the experimental results of Cornubert and co-workers [14] for the action of concentrated hydrochloric acid on 1-methylcyclohexanol-2 (cis- and trans-forms). In the dehydrochlorination of the methylcyclohexanes obtained by reaction of 1-methylcyclohexanol-3 and 1-methylcyclohexanol-4 with hydrochloric acid, substantially the sole product is 1-methylcyclohexene-3 (nearly quantitative yield). This shows that the two methylcyclohexanols are converted by reaction with hydrochloric acid into the same product - 1-methyl-4-chlorocyclohexane.

EXPERIMENTAL

Chlorination of methylcyclohexane. The initial methylcyclohexane had b.p. 100.5° (760 mm), n_D^{20} 1.4231, and d_4^{20} 0.7693. It was chlorinated in a pear-shaped flask fitted with mechanical stirrer, thermometer, and a sealed-in chlorine inlet tube extending nearly to the bottom of the flask. This tube terminated in a perforated bulb through

TABLE 1. Results of Typical Experiments on Chlorination of Methylcyclohexane

Expt. no.	Experimental temperature, °C	Duration of experiment, hr	Degree of conversion of hydrocarbon, weight %	Yield of chlorides in wt. % of theoretical yield calculated on reacted hydrocarbon		
				Monochloro derivatives	Dichloro derivatives	Trichloro derivatives, probably containing some dichloro derivatives
1	60	5,0	58,0	64,4	12,0	1,7
2	60	8,0	68,5	53,3	19,0	2,6
3	20	2,0	29,5	81,0	12,3	3,3
4	20	2,0	30,0	79,0	11,4	2,3
5	20	2,0	30,3	79,0	10,5	3,2

TABLE 2. Properties of Chlorinated Methylcyclohexanes

Methylchlorocyclohexanes	B. p., °C (p mm Hg)	n_D^{20}	d_4^{20}	Chlorine content, %	
				calculated	found
a) Methylchlorocyclohexanes obtained in chlorination of methylcyclohexane	67,5—70,5(40)	1,4582	0,9701	26,74	26,64
b) Methylchlorocyclohexanes obtained in chlorination of methylcyclohexane	62—70(10)	1,4852	1,1367	42,5	42,1
	70—75(10)	1,4865	1,1412	42,5	42,1
	75—80(10)	1,4890	1,1532	42,5	42,5
	80—90(10)	1,4935	1,1762	42,5	43,0
c) Methylchlorocyclohexanes obtained by the action of conc. hydrochloric acid					
on 1-methylcyclohexanol-2	67—68(40)	1,4580	0,9717	26,74	26,0
on 1-methylcyclohexanol-3	68—68,2(40)	1,4580	0,9684	26,74	26,0
on 1-methylcyclohexanol-4	68—69(40)	1,4580	0,9697	26,74	26,6

which the chlorine could enter the reaction mixture in the form of fine bubbles. The reaction was carried out in the liquid phase at room temperature in diffused daylight. Each experiment was performed with 1 M (98.1 g) of hydrocarbon. Chlorine was introduced from a cylinder at a rate of 75 ml per minute. The temperature and duration of chlorination were varied in different experiments. Nitrogen was blown for 30 min through the chlorination product for elimination of the main bulk of dissolved hydrogen chloride. The reaction mixture was then washed with water, with 10% sodium carbonate solution, and again with water until neutral. The chlorination products, after drying, were fractionally distilled in a 24-plate column at 40 mm. Results of chlorination of methylcyclohexane are set forth in Table 1. The physicochemical properties of the chloro derivatives are set forth in Table 2.

The data of Table 1 show that the highest yields of methylchlorocyclohexanes are attained in chlorinations at room temperature and with reaction periods of 2 hr. Properties of methylchlorocyclohexanes prepared by us from individual methylcyclohexanols by the action of excess of concentrated hydrochloric acid (s.g. 1.19) with heating to 70° for 15 hr are set forth in Table 2. We prepared the isomeric methylcyclohexanols by hydrogenation of the corresponding pure cresols in an autoclave at 180–200° and a hydrogen pressure of 100–120 atm in presence of skeletal nickel-aluminum catalyst.

Dehydrochlorination of methylchlorocyclohexanes. Experiments on dehydrochlorination of methylchlorocyclohexanes, characterized in Table 2, were carried out at 220° in a flow apparatus. Methylchlorocyclohexanes were admitted at a rate assumed equivalent to a space velocity of 1.0 hr⁻¹. Catalysts were barium chloride, deposited on activated birch carbon in the proportion of 5–10 weight-%, or simply active carbon alone. Results are set forth in Table 3.

TABLE 3. Results of Dehydrochlorination of a Mixture of Methylchlorocyclohexanes.

Expt. no.	Catalyst	Experimental temperature, °C	Degree of dehydrochlorination, %	Composition of catalyzate weight - %		
				methylcyclohexenes	dimethylcyclopentenes	unchanged monochloride
1	10% BaCl ₂ on active carbon	300	92.0	78.5	10.3	11.2
2	The same	220	88.7	77.6	—	22.4
3	5% BaCl ₂ on active carbon	220	80.0	70.0	—	30.0
4	The same	220	72.0	63.0	—	37.0
5	Active birch carbon .	220	76.0	63.9	—	36.1

We see from the data of Table 3 that at 300° in presence of 10% BaCl₂ on active carbon, the removal of the elements of hydrogen chloride from the molecule of methylchlorocyclohexane is accompanied by contraction of the

six-membered ring to a five-membered ring. The content of five-membered cyclenes was determined by Zelinskii's method (involving successive hydrogenation and dehydrogenation) followed by chromatographic separation of the hydrides from the aromatic hydrocarbons on silica gel. The isolated fraction of hydrides boiled at 99.9-101.5° (760 mm) and had n_D^{20} 1.4125 and d_4^{20} 0.7698. Judging by the properties [15], this fraction contains 1, 2-dimethylcyclopentane (cis- and trans-forms). The presence of five-membered cyclenes was also confirmed by the Raman spectrum*. Five-membered cyclenes were not detected in catalyzates from dehydrochlorination experiments at 220°.

Investigation of products of dehydrochlorination of methylchlorocyclohexanes. After preliminary purification, the products of dehydrochlorination were subjected to distillation for separation of the methylcyclohexenes from unreacted methylchlorocyclohexanes. The isolated methylcyclohexenes were then subjected to careful fractionation in a 24-plate column. The following narrow cuts of methylcyclohexenes were collected: fraction I, b.p. 100-104° (745 mm), n_D^{20} 1.4425, d_4^{20} 0.8005; fraction II, b.p. 104-108° (745 mm), n_D^{20} 1.4470; d_4^{20} 0.8044; fraction III, b.p. 108-110° (745 mm), n_D^{20} 1.4508; d_4^{20} 0.8118.

It was of interest to subject the various fractions to gas-liquid chromatographic analysis in the apparatus described earlier [16]. With this objective we isolated in the pure form 1-methylcyclohexene-1 with b.p. 108-109° (748 mm), n_D^{20} 1.4505, d_4^{20} 0.8088, and 1-methylcyclohexene-3 with b.p. 100-100.8° (742 mm), n_D^{20} 1.4420, d_4^{20} 0.7999. The former was isolated by careful fractional distillation in a column of fraction II with b.p. 108-110° (745 mm). The second substance was obtained in almost quantitative yield by fractional distillation of the catalyzate formed by dehydrochlorination of the products of reaction of concentrated hydrochloric acid with 1-methylcyclohexanol-3 and 1-methylcyclohexanol-4. A comparison of the constants of the narrow cuts of dehydrochlorination

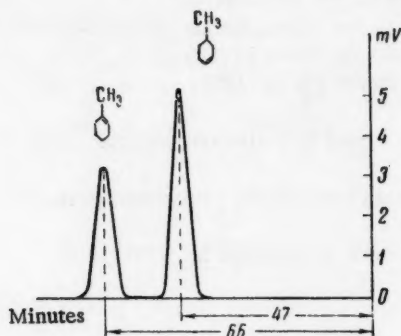


Fig. 1. Results of chromatographic resolution of an artificial mixture of 1-methylcyclohexene-1 and 1-methylcyclohexene-3.

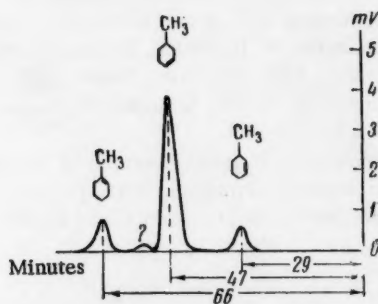


Fig. 2. Results of chromatographic resolution of a mixture of methylcyclohexenes obtained by dehydrochlorination of the product of reaction of 1-methylcyclohexanol-2 with hydrochloric acid.

catalyzates with those of pure methylcyclohexenes indicates that fraction I contains mainly 1-methylcyclohexene-3, and fraction III consists of 1-methylcyclohexene-1. Fraction II is intermediate in composition. Artificial mixtures of pure 1-methylcyclohexene-1 and 1-methylcyclohexene-3 were made up in connection with the chromatographic analysis of methylcyclohexenes formed by dehydrochlorination of the methylchlorocyclohexanes resulting from chlorination of methylcyclohexane. The optimum conditions for resolution of the experimental mixtures were established beforehand with the help of the artificial mixtures. It was found that at 60° and with a hydrogen admission rate of 50-55 ml/min, the mixture of methylcyclohexenes is completely resolved in the course of 70 min. The volume of the samples analyzed did not exceed 0.5 ml. Figs. 1 and 2 illustrate the results of chromatographic resolution of mixtures of 1-methylcyclohexene-1 and 1-methylcyclohexene-3.

* The authors thank G. K. Gaivoronskaya for carrying out the spectral analysis.

SUMMARY

1. Conditions were established for smooth dehydrochlorination of methylchlorocyclohexanes to methylcyclohexenes in yields of 63 to 77%.
2. The main products of catalytic dehydrochlorination of a mixture of methylchlorocyclohexanes obtained by direct chlorination of methylcyclohexane were 1-methylcyclohexene-1 (24.5-42.0%) and 1-methylcyclohexene-2 (58.75.5%).

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DEHYDROGENATION OF 2,2,4-TRIMETHYLPENTANE OVER ALUMINA-CHROMIA-POTASH CATALYST

E. A. Timofeeva, N. I. Shuikin, and T. P. Dobrynina

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

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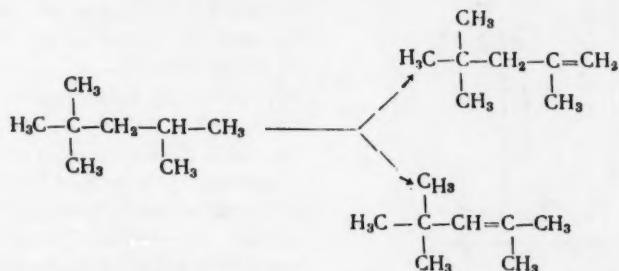
pp. 863-867, May, 1961

Original article submitted April 20, 1960

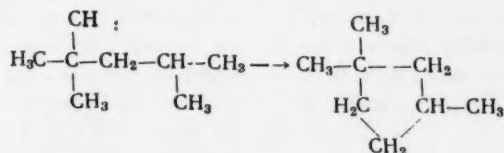
Several publications have dealt with the various transformations of 2, 2, 4-trimethylpentane in presence of oxide catalysts. The first investigators [1-3] carried out experiments at temperatures of 465-480° and the catalysts were chromium oxide, chromium oxide on alumina, vanadium pentoxide on alumina, etc. The resulting catalyzates contained a high proportion of alkenes (up to 26% in some cases) and only 1-3% of aromatic hydrocarbons. In experiments at 510-550°, other workers [4-9] found in the isooctane catalyzates very much larger amounts of aromatic hydrocarbons (up to 50%) but only 1-16% of alkenes (the actual quantity depending on the type of catalyst and the experimental conditions). The authors of the cited papers, as well as Herington and Rideal [10], were interested mainly in the structure of the resulting aromatic hydrocarbons. The main bulk usually comprised p- and m- (or o-) xylenes or all three isomers. Benzene [8], toluene [8,9], and naphthalene [8] were sometimes detected in the catalyzates.

The structure of the alkenes formed from 2, 2, 4-trimethylpentane has not previously been investigated. Little attention has moreover been paid to the composition of the paraffinic component of isooctane catalyzate. Obolentsev and Usov [5] point out that 2, 5-dimethylhexane might be one of the products of transformation of isooctane. Platě and Golovina [8] tried to detect cyclopentane hydrocarbons as well as isomers of 2, 2, 4-trimethylpentane in isooctane catalyzates. However in the paraffinic portion of the catalyzate they found only 2, 4-dimethylpentane apart from unchanged isooctane.

We set ourselves the task of investigating the dehydrogenation of 2, 2, 4-trimethylpentane in presence of alumina-chromia-potash catalyst which had exhibited great activity in the dehydration of pentanes [11]. In the examination of the composition of the catalyzates we paid special attention to the unsaturated and paraffinic hydrocarbons. It was established that the alkenes in the liquid part of the catalyzate consist predominantly of 2, 4, 4-trimethylpentene-1 and 2, 4, 4-trimethylpentene-2. These are the two theoretically possible isomers:



In the paraffinic part of the catalyzate we found, apart from unchanged isooctane, 1, 1, 3-trimethylcyclopentane:



This provided further confirmation of our earlier demonstration [12-15] of the possibility of fusion of alkanes to the corresponding five-membered cyclanes over oxide catalysts. Dehydrocyclization of *n*-alkanes to the corresponding cyclopentane hydrocarbons over Pt-C was previously reported by Kazanskii, Liberman and co-workers [16]; they also described the dehydrocyclization of isooctane to 1, 1, 3-trimethylcyclopentane over this catalyst [17-19].

EXPERIMENTAL

After distillation in a column over metallic sodium, the 2, 2, 4-trimethylpentane had constants agreeing with those reported in the literature [20]. The composition and method of preparation of the alumina-chromia-potash catalyst 6, with which we worked has been described in one of our papers [21]. The experimental procedure and the analytical method are also described in the same paper. In each experiment 100 ml of hydrocarbon was passed over 30 ml of catalyst. The content of unsaturated and aromatic hydrocarbons in the catalyzates was determined. Some fractions were also examined by Raman spectrography and by gas-liquid chromatography. Three sets of experiments were carried out: 1) At 450° and a space velocity of 0.3 hr⁻¹; 2) at 500° and a space velocity of 0.5 hr⁻¹; 3) at 550° and a space velocity of 1.1 hr⁻¹.

Analysis of catalyzate obtained in experiments at 450° and a space velocity of 0.3 hr⁻¹. The catalyzate was obtained in a yields of 97.0%; n_D^{20} 1.3930. The iodine value determination indicated an olefin content of 18.7%. Traces of aromatics were also detected. From 100 ml of isooctane was isolated 3.10 liters of gas which contained 89.8% of hydrogen, 4.2% of unsaturated hydrocarbons, and 6.0% of saturated hydrocarbons. The catalyzate (80 ml) was separated into two parts with the help of silica gel: 1) A paraffinic fraction with b.p. 98.4-98.9° and n_D^{20} 1.3910; the Raman spectrum showed the presence of unchanged isooctane; 2) a concentrate of alkanes boiling in the range of 98.0 to 109.0° with n_D^{20} 1.4080; this contained 66% of unsaturateds. The Raman spectrum revealed the presence of 2, 4, 4-trimethylpentene-1, 2, 4, 4-trimethylpentene-2, 2, 4-dimethylhexane, and isooctane. Under our conditions 2, 2, 4-trimethylpentane is consequently dehydrogenated relatively smoothly with formation of 19% of the corresponding theoretically possible alkenes.

Analysis of catalyzate obtained in experiments at 500° and space velocity of 0.5 hr⁻¹. The yield of catalyzate with n_D^{20} 1.400 was 93.1%; iodine number 76.6. During the catalytic operation 100 ml of isooctane gave 11.86 liters of gases composed of 91.6% hydrogen, 4.2% methane, 0.3% ethane, 0.6% propane, 0.4% isobutane, 1.5% *n*-butane, and 1.4% pentanes. The catalyzate was subjected to debutanization in a 40-plate column. This operation gave 4.48 liters of gas, equivalent to 15.9% of the total weight of catalyzate. This gas contained 2.6% hydrogen, 0.3% methane, 0.2% ethane, traces of ethylene, 1.1% propane, 43.0% butane + isobutane, 45.2% butylenes + isobutylenes, and 7.7% C₅ hydrocarbons. The high proportion of C₄ hydrocarbons (about 90%) in the gas indicates that under the experimental conditions the isooctane molecule is cleaved mainly into two parts predominantly in the middle. The debutanized liquid catalyzate had n_D^{20} 1.4010 and iodine number 42.2; the content of alkenes, calculated as C₈, was 18.6%. The content of aromatics was 9.0%. The catalyzate (100 ml) was subjected to chromatographic resolution on silica gel by the technique of Topchiev and co-workers [22]. Five fractions were obtained: 1) paraffinic, 71.5 ml with n_D^{20} 1.3918, boiling range 98.6-103.3°; 2) intermediate, 2.0 ml with n_D^{20} 1.3023; 3) olefinic, 17.0 ml with n_D^{20} 1.4150, boiling range 90.0-106.5°, containing 100% of olefins calculated as C₈; 4) intermediate, 1.6 ml with n_D^{20} 1.4776; 5) aromatic, 7.0 ml with n_D^{20} 1.4928, boiling range 110.0-138.7°, containing 85.0% of aromatics and 11.2% of unsaturateds. Examination of the Raman spectrum of the catalyzate revealed the presence of 1, 1, 3-trimethylcyclopentane in addition to unchanged isooctane. Analysis of the fraction by gas-

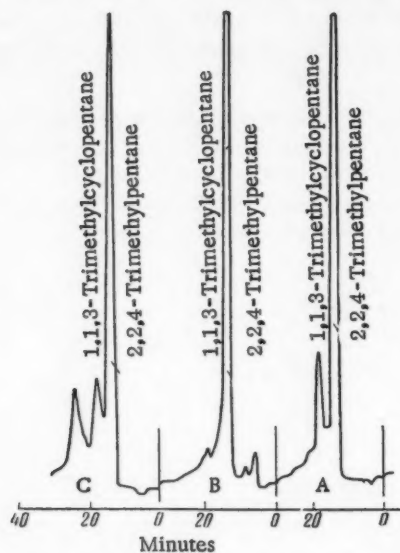


Fig. 1. Chromatograms: A) mixtures of 1, 1, 3-trimethylcyclopentane and 2, 2, 4-trimethylpentane; B) paraffinic portion of 2, 2, 4-trimethylpentane catalyzate obtained at 500° and space velocity of 0.5 hr⁻¹; C) the same at 550° and space velocity of 1.1 hr⁻¹.

liquid chromatography confirmed these findings (Fig. 1, chromatograms A and B). Judging by the Raman spectrum, the olefinic portion of the catalyzate contained 2, 4, 4-trimethylpentene-1 and 2, 4, 4-trimethylpentene-2. On the basis of the chromatogram (Fig. 2) it can be assumed that the lower boiling hydrocarbon (2, 4, 4-trimethylpentene-1) is present to the extent of only 10%, the remaining 90% being 2, 4, 4-trimethylpentene-2. The aromatic hydro-



Fig. 2. Chromatogram of olefinic portion of 2, 2, 4-trimethylpentane catalyzate obtained at 500° and space velocity of 0.5 hr⁻¹.

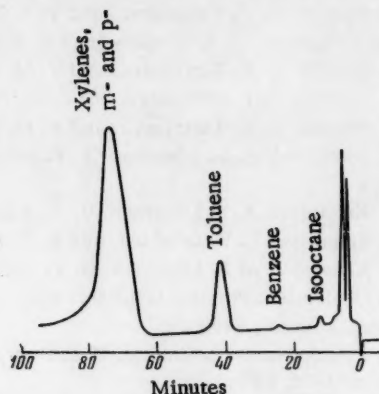


Fig. 3. Chromatogram of aromatic portion of 2, 2, 4-trimethylpentane catalyzate obtained at 500° and space velocity of 0.5 hr⁻¹.

carbons in the catalyzate were xylenes (87%) (o-xylene absent), toluene (13%), and benzene (traces, as evident from Fig.3).

Analysis of catalyzate obtained at 550° and a space velocity of 1.1 hr⁻¹. Under these conditions the yield of catalyzate was 79.8%; after debutanization it had n_D^{20} 1.4065, iodine number 60.4, content of unsaturateds (calculated as C₈) 26.6%; content of aromatics 9.9%. Alkenes and aromatics were removed from the catalyzate by treatment successively with sulfuric acid (first dilute and then concentrated) and 2% oleum. A 98.5-109.0° fraction with n_D^{20} 1.3950 was isolated from the paraffinic portion of the catalyzate; this represented 7% of the total paraffinic portion or 4.3% of the debutanized catalyzate. Judging by the Raman spectrum this fraction contained 1, 1, 3-trimethylcyclopentane in addition to unchanged isooctane. The presence of 10-15% of cyclopentane hydrocarbon in the 98.5-109.0° fraction was also demonstrated by gas-liquid chromatography (see Fig. 1, chromatogram B).

SUMMARY

1. Dehydrogenation of 2, 2, 4-trimethylpentane was investigated under various conditions over alumina-chromia-potash catalyst.
2. At 450° and a space velocity of the isooctane of 0.3 hr⁻¹, this reaction is highly selective and gives 18.7% of alkenes comprising 2, 4, 4-trimethylpentene-1 and 2, 4, 4-trimethylpentene-2.
3. At 500° and a space velocity of 0.5 hr⁻¹, the products—apart from 2, 4, 4-trimethylpentene-1 and 2, 4, 4-trimethylpentene-2 (totalling 18.6% of the catalyzate)—are 9% of aromatic hydrocarbons comprising xylenes, toluene, and traces of benzene.
4. At 500-550° 2, 2, 4-trimethylpentane over alumina-chromia-potash catalyst fuses to 1, 1, 3-trimethylcyclopentane.

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DEALKYLATION OF MESITYLENE AND ASSOCIATED ALKYLATION OF BENZENE AND TOLUENE IN PRESENCE OF SYNTHETIC ALUMOSILICATES

A. V. Topchiev, G. M. Mamedaliev, and L. S. Kovaleva

Institute of Petrochemical Synthesis, Academy of Sciences, USSR

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Dealkylation of xylenes and the associated alkylation of benzene in presence of aluminum chloride [1-7], and also of natural and synthetic aluminosilicates [8,9] has been studied in the works of a series of authors. These investigations had as their goal the development of a method of industrial production of toluene. Latterly, in connection with the widespread development of the production of a whole series of synthetic materials, the isomeric xylenes have achieved exceedingly important practical significance. One of the prospective methods for p-xylene production, as has already been noted by us [10-12] and subsequently by other authors [13-16], is the isomeric conversion of m- and o- xylenes into the para- isomer, achieved comparatively easily in presence of synthetic aluminosilicates under atmospheric pressure and in vacuo.

In our works it has been shown that the xylenes can be synthesized by dealkylation and associated alkylation of aromatic hydrocarbons derived from polyalkylbenzene sources included in the products of pyrolytic coke-gas production and of industrial aromatizing reformation of narrow gasoline fractions [17,18]. Thus, on catalytic treatment of a mixture of toluene and the solvent from coke-gas production (mainly a mixture of pseudocumene, mesitylene and

TABLE 1. Properties of Products of Catalytic Treatment of a Mixture of Benzene and Mesitylene (temperature 480°; flow rate 0.5 hour⁻¹)

Fractional composition	Raw material mesitylene: benzene=1:2	Expt. 233, atmospheric	Expt. 232, 5 atm	Expt. 421, 10 atm	Expt. 235, 15 atm
Commencement of boiling	79	74	71	78	62
C.b. — 78	—	4.45	1.83	—	0.34
78—83	64—69	55.57	51.06	49.41	45.68
83—88		0.70	0.50	0.19	0.36
88—103		1.66	0.71	0.67	0.85
103—108		0.98	1.05	0.49	0.79
108—113		1.77	11.21	18.72	22.32
113—118	0.72	0.18	0.53	0.24	0.35
118—125		0.56	0.48	0.33	0.42
125—136		1.42	0.81	1.09	3.21
136—144		6.64	15.40	16.21	14.01
144—149		0.18	0.63	0.63	0.46
149—160		0.88	1.16	0.97	0.92
160—165	29.90	4.38	1.87	1.29	1.07
165—175	—	14.63	5.64	3.43	3.05
End of boiling, °C	165.5	172.3	167.5	168	169.5
Total yield, wt. %	98.77	94.00	92.88	93.61	93.83
Residue, wt. %	3.46	3.04	4.81	4.76	3.20
Losses, wt. %	1.33	2.96	2.31	1.78	2.97
Material balance, wt. %					
Catalyzate	—	97.3	93.4	93.7	91.2
Coke	—	0.9	2.4	3.6	4.6
Gas	—	1.8	1.8	1.1	1.9
Losses	—	1.8	2.4	1.6	2.3

TABLE 2. Properties of Basic Aromatic Fractions

Properties of fractions	Raw material mesitylene benzene =1:2	Expt. 233	Expt. 232	Expt. 421	Expt. 235
Fraction 78-83°					
Yield, wt. %	63,69	55,57	51,06	49,41	45,68
n_D^{20}	1,5017	1,5000	1,4984	1,5009	1,5014
d_4^{20}	0,8776	0,8741	0,8731	0,8743	0,8779
Iodine number	0	0	0	0	0
Fraction 108-113°					
Yield, wt. %	—	1,77	11,21	18,72	22,32
n_D^{20}	—	1,4985	1,4975	1,4978	1,4982
d_4^{20}	—	—	0,8672	0,8668	0,8676
Iodine number	—	0	0	0	0
Fraction 136-144°					
Yield, wt. %	—	6,64	15,40	16,21	14,01
n_D^{20}	—	1,4991	1,4990	1,4990	1,4990
d_4^{20}	—	0,8659	0,8674	0,8656	0,8684
Iodine number	—	0,3	0	0	0
Fraction 160-165°					
Yield, wt. %	29,90	4,38	1,87	1,29	1,07
n_D^{20}	1,4995	1,5043	1,5029	1,5015	1,5013
d_4^{20}	0,8663	0,8749	—	—	—
Iodine number	0	0	0	—	—
Fraction 165-175°					
Yield, wt. %	—	14,63	5,64	3,43	3,05
n_D^{20}	—	1,5051	1,5049	1,5032	1,5045
d_4^{20}	—	0,8743	0,8745	—	0,8754
Iodine number	—	0	0	0	0

hemimellitol) under optimum temperature and pressure conditions, yield of xylenes in one operation amounted to 28% [19]. This process consists of a complex of a number of reactions occurring together and interdependently: dealkylation, alkylation, dismutation, and isomeric conversions of initial aromatic compounds.

In studying these reactions it was expedient to carry out an experimental investigation on conversion of individual alkylaromatic hydrocarbons. A study had been made previously of demethylation and alkyl group transfer of pseudocumene in presence of toluene and benzene over synthetic aluminosilicates. It was shown that on catalytic treatment of a mixture of pseudocumene and benzene, dealkylation of pseudocumene and associated alkylation of benzene took place mainly, with formation of ~20% toluene and ~17% xylenes. Similar conversions were observed on treating a mixture of pseudocumene and toluene. In the present communication results are given of an investigation of dealkylation, transfer of mesitylene methyl groups and associated alkylation of benzene and toluene in presence of synthetic aluminosilicates.

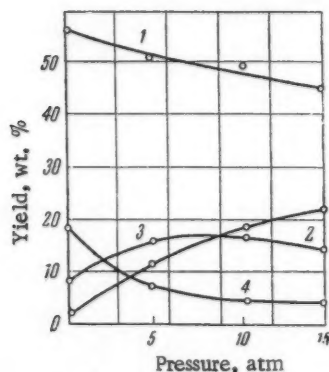


Fig. 1. Relationship between aromatic hydrocarbon yield and pressure during treatment of a benzene-mesitylene mixture: 1) benzene; 2) toluene; 3) xylenes; 4) trimethylbenzenes.

EXPERIMENTAL

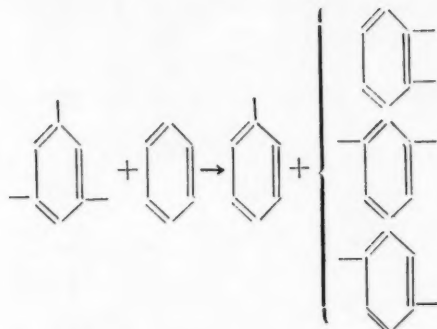
As the initial products the following were used: mesitylene (boiling range 164.5-164.8°; n_D^{20} 1.5002; d_4^{20} 0.8668), cryoscopic benzene (78.5-80°; n_D^{20} 1.5012, d_4^{20} 0.8790), toluene (109.9-111°; n_D^{20} 1.4970, d_4^{20} 0.8669).

Experiments were carried out in circulatory reactor equipment with a stationary catalyst layer, the scheme and description of which were given in the work [18]. Spectral investigations of basic products of mesitylene conversion were carried out in the laboratory of physicochemical investigation methods by A. N. Kisilinskii.

Demethylation of Mesitylene and Associated Methylation of Benzene. A mixture of mesitylene and benzene in the ratio by weight 1:2 was subjected to catalytic treatment. The product was passed once over the catalyst at a temperature of 480°, flow rate 0.5 hour⁻¹ and various pressures. The material balance of the process, properties of the initial mixture and the catalyzates obtained from its treatment and their basic aromatic fractions are given in Tables 1 and 2. Curves showing relationship between aromatic hydrocarbon yield and pressure are given in Fig. 1.

At atmospheric pressure yield of reaction products amounted to 97.3%, gas - formation was practically unobserved, coke deposits on catalyst amounted to 0.9%. Even under these conditions a certain amount of mesitylene dealkylation and associated benzene alkylation was observed. Yield of toluene fraction amounted to 1.7%, of xylenes - 7%. Increase of pressure to 5 atm. noticeably intensified the reaction direction intended. As a result of intensification of transfer of the methyl group from the mesitylene molecule to the benzene molecule, content of toluene and xylene fraction in the catalyzate increased respectively to 11.2 and 15.4%. Yield of catalyzate amounted to ~ 93%, of gas - 1.8%, of coke - 2.4%. At 10 atm. pressure yield of toluene and xylene fraction increased and amounted to 18.7 and 17% respectively. Amount of benzene fraction decreased from ~ 64% in the initial mixture to ~ 49% in the catalyzate, trimethylbenzene fraction from ~ 30% to 4.5%. At 15 atm. pressure the process was characterized by comparatively large coke - and gas- formation (4.6 and 1.9% respectively). Yield and quality of basic aromatic fractions did not differ substantially from the data of the experiment carried out at 10 atm.

At a temperature of 480° and 5-10 atm. pressure catalytic treatment of a mixture of mesitylene and benzene over aluminosilicates resulted mainly in mesitylene dealkylation and associated benzene alkylation



In addition, under the experimental conditions isomeric conversions of mesitylene took place, as a result of which the trimethylbenzene fractions of the catalyzate were characterized by a high pseudocumene content.

Demethylation of Mesitylene and Associated Methylation of Toluene. A mixture of toluene and mesitylene in the ratio by weight 2:1 was subjected to catalytic treatment. Analytic data on the catalyzates obtained and their basic aromatic fractions are given in Tables 3 and 4. Experiments were carried out at a temperature of 480°, rate of raw material inflow 0.5 hour⁻¹ and various pressures. Curves showing relationship between yield of toluene, xylenes, trimethylbenzenes, and pressure are given in Fig. 2.

At atmospheric pressure yield of catalyzate yield amounted to 99.4%, gas-formation was not observed, and yield of coke-like reaction products did not exceed 0.4%. As a result of mesitylene dealkylation and associated toluene alkylation ~ 14% of xylenes was formed, as a result of which content of toluene and trimethylbenzene fractions decreased respectively from 65.3 and 31.1% in the initial mixture to 56.7 and 20.1% in the catalyzate. Increase in pressure to 3-5 atm. led to increase in yield of xylene fraction to 26.7 and 32% respectively. At the same time, as a result of partial hydrocracking of side chains of initial and resulting aromatic hydrocarbons, formation of ~ 2-3% benzene was observed.

Further increase in pressure to 10 atm. had no substantial effect on yield of basic aromatic hydrocarbons.

Several experiments were carried out at 5 atm. pressure over the temperature range 425-480°. In Fig. 3 is shown the relationship between yield of basic aromatic catalyzate fractions and temperatures. At 425° xylene fraction yield amounts to 26% as against 30% at 480°. Further decrease in temperature depresses methyl group transfer, and the catalyzate is characterized by comparatively low xylene content.

TABLE 3. Properties of Products of Catalytic Treatment of a Mixture of Toluene

Fractional composition and properties of product	Raw ma- terial, me- sitylene: toluene = = 1 : 2	Temperature 480°		
		atmospheric	3 atm	5 atm
		expt. 219	expt. 221	expt. 220
Commencement of boiling, °C	106	75	53	75
C. b. -78	—	Yield of fraction, wt. %		
78—83	—	0,18	0,23	0,27
83—88	—	0,33	2,69	3,03
88—103	—	0,20	0,24	0,13
103—108	0,26	0,56	0,78	0,65
108—113	65,32	0,90	0,50	1,14
113—118	0,10	56,70	50,73	43,04
118—125	0,17	0,24	0,18	0,56
125—136	0,25	0,25	0,72	0,71
136—144	0,13	0,67	0,55	2,21
144—149	0,16	13,93	26,69	30,01
149—160	0,68	0,48	0,88	0,63
160—165	31,11	0,93	0,96	1,06
165—175	—	3,86	2,75	1,62
175—185	—	17,33	8,95	10,36
End of boiling, °C	164,8	—	—	0,96
Total yield, wt. %	98,18	173	171	176
Residue	1,70	96,56	96,46	96,38
Losses	0,12	1,72	2,71	3,00
Material balance, wt. %	—	1,72	0,80	0,62
Catalyzate	—	99,41	95,7	94,2
Coke	—	0,38	2,3	2,6
Gas	—	0,21	2,0	1,8
Losses	—	—	—	1,4

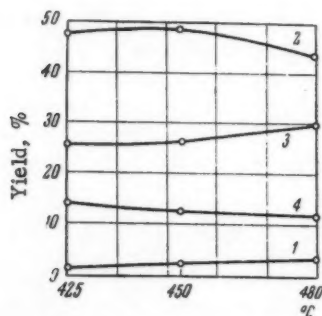
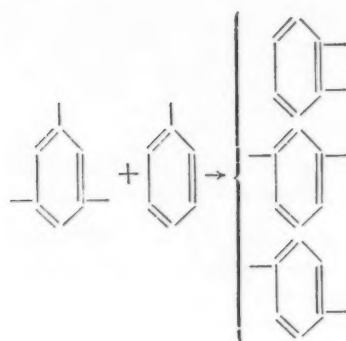


Fig. 3. Relationship between yield of basic aromatic fractions and temperature: 1) benzene; 2) toluene; 3) xylenes; 4) trimethylbenzenes.

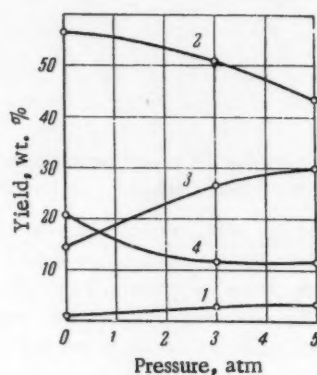


Fig. 2. Relationship between yield of aromatic hydrocarbons and pressure in treatment of a toluene-mesitylene mixture: 1) benzene; 2) toluene; 3) xylenes; 4) trimethylbenzenes.

Results of investigations carried out showed that under optimum conditions (480°; 5 atm. pressure; flow rate 0.5 hr^{-1}) treatment of a mixture of toluene and mesitylene over aluminosilicate was characterized mainly by occurrence of mesitylene demethylation and associated toluene methylation with formation of 30-32% of a mixture of xylenes. According to spectral analytical data, the catalyzate xylene fraction consisted of a mixture of ~50% m-xylene, ~20% p-xylene and ~30% o-xylene. As a result of isomeric mesitylene

TABLE 4. Properties of Basic Aromatic Fractions

Properties of fractions	Raw material mesitylene: toluene = 1:2	Expt. 219	Expt. 221	Expt. 220
Fraction 78-83°				
Yield, wt. %	—	0,33	2,69	3,03
n_D^{20}	—	1,4904	1,4990	1,4990
d_4^{20}	—	—	0,8741	—
Iodine number	—	—	0	2.2
Fraction 108-113°				
Yield, wt. %	65,32	56,70	50,37	43,04
n_D^{20}	1,4977	1,4977	1,4980	1,4978
d_4^{20}	0,8660	0,8678	0,8656	0,8652
Iodine number	0	0	0	0
Fraction 136-144°				
Yield, wt. %	—	13,93	26,69	30,01
n_D^{20}	—	1,4998	1,4999	1,4990
d_4^{20}	—	0,8675	0,8660	0,8666
Iodine number	—	0	0	0
Fraction 160-165°				
Yield, wt. %	31,11	3,86	2,75	1,62
n_D^{20}	1,5004	1,5013	1,5018	1,5017
d_4^{20}	0,8756	0,8700	0,8686	—
Iodine number	0	0	0	0
Fraction 165-175°				
Yield, wt. %	—	17,33	8,95	10,36
n_D^{20}	—	1,5058	1,5054	1,5048
d_4^{20}	—	0,8764	0,8757	0,8731
Iodine number	—	0,8	0,7	0

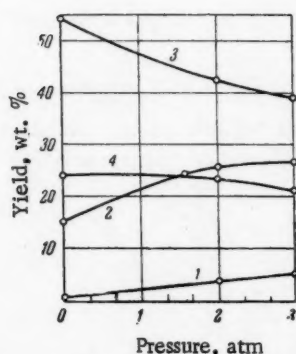


Fig. 4. Relationship between yield of aromatic hydrocarbons and pressure during treatment of mesitylene: 1) toluene; 2) xylenes; 3) trimethylbenzenes; 4) tetramethylbenzenes.

At atmospheric pressure ~40% of the initial mesitylene underwent dismutation with formation of 16% xylenes and 24% tetramethylbenzenes. Yield of liquid reaction products amounted to 94%, of gas—1.4%, of coke—1.6%. Increase in pressure noticeably intensified disproportionation of mesitylene methyl groups. In addition, partial mesi-

conversion the resulting trimethylbenzene fraction of the catalyzate contained a considerable amount of pseudo-cumene. In this case, mesitylene dismutation was practically unobserved.

Methyl Group Transfer and Isomeric Mesitylene Conversion. Catalytic treatment of mesitylene in presence of benzene and toluene, as has been shown, was characterized by occurrence of demethylation and associated methylation of initial aromatic hydrocarbons. Presence of benzene and toluene depressed mesitylene dismutation and appreciable formation of tetramethylbenzenes was not observed.

A series of experiments was carried out on catalytic treatment of mesitylene. The material balance of the process and results of analysis of resulting catalyzates and their aromatic fractions are given in Tables 5 and 6. Curves showing relationship between yield of basic conversion products and pressure are given in Fig. 4.

TABLE 5. Properties of Products of Catalytic Mesitylene Conversion (flow rate 0.5 hour⁻¹)

Fractional composition and product properties	Temperature 480°				Temperature 400°
	atmos- pheric	2 atm	3 atm	5 atm	3 atm
	expt. 223	expt. 231	expt. 228	expt. 226	expt. 236
Commencement of boiling, °C	109,5	90	84,5	83,5	80,5
	Yield of fraction, wt. %				
C.b. — 88	—	—	0,14	0,17	0,11
88—103	—	0,52	0,50	0,15	0,33
103—108	—	0,35	0,29	0,30	0,23
108—113	0,30	3,77	5,11	2,50	0,61
113—118	0,33	0,16	0,31	0,22	0,22
118—125	0,42	0,39	0,37	0,49	0,34
125—136	0,56	0,86	1,27	1,04	0,77
136—144	15,90	25,52	26,52	23,68	15,63
144—149	0,88	0,13	0,83	0,33	0,63
149—162	2,38	1,26	1,61	4,31	1,61
162—167	21,31	11,94	12,75	26,86	15,72
167—172	30,74	26,59	23,00	12,76	35,21
172—180	2,88	4,09	3,40	2,79	3,16
End of boiling	180	180	180	180	180
Total yield, wt. %	75,70	75,58	76,10	75,60	74,57
Residue	24,05	23,47	20,72	22,61	24,98
Losses	0,25	0,95	3,18	1,79	0,45
Material balance, wt. %					
Catalyzate	94,4	90,8	83,6	84,7	97,0
Coke	1,6	4,8	7,3	9,9	0,7
Gas	1,4	4,2	6,4	5,1	—
Loses	2,6	0,2	2,7	0,3	2,3

tylene cracking occurred with formation of 4-5% toluene. At 2 atm. yield of xylene fraction amounted to 25%, of tetramethylbenzene to ~ 23%. With increase in pressure, a noticeable increase was observed in yield of coke-like and gaseous reaction products.

At 3 atm. decrease in temperature to 400° depressed mesitylene hydrocracking, and in addition lowered the dismutation effect somewhat. Yield of xylene and tetramethylbenzenes amounted to ~ 17% and ~ 25%. Catalyzate composition in this experiment was practically identical to the composition of the catalyzate obtained at atmospheric pressure and 480°.

According to spectral analytical data, the xylene consisted of a mixture of ~ 45% m-xylene, ~ 25% o-xylene.

Thus, catalytic mesitylene conversion over aluminosilicates at 480° and 2-3 atm. pressure was characterized mainly by disproportionation of methyl groups with formation of xylenes and tetramethylbenzenes:

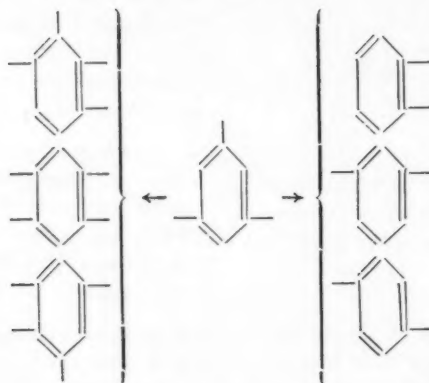
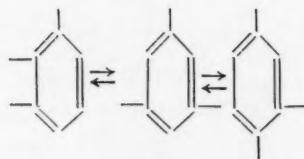


TABLE 6. Properties of Basic Aromatic Fractions of Products of Mesitylene Conversion

Properties of fraction	Expt. 223	Expt. 231	Expt. 228	Expt. 226	Expt. 236
Fraction 108-113°					
Yield, wt. %	0,30	3,77	5,11	2,50	0,61
n_D^{20}	1,4942	1,4952	1,4961	1,4959	1,4880
d_4^{20}	—	0,8659	0,8636	0,8666	—
Iodine number	—	0,28	0	1,2	—
Fraction 136-144°					
Yield, wt. %	15,90	25,52	26,52	23,68	15,63
n_D^{20}	1,4990	1,4999	1,4998	1,4990	1,4982
d_4^{20}	0,8692	0,8678	0,8662	0,8662	0,8628
Iodine number	0	0,20	0	1,5	0,5
Fraction 162-167°					
Yield, wt. %	21,31	11,94	12,75	26,86	15,72
n_D^{20}	1,5018	1,5040	1,5020	1,5040	1,5006
d_4^{20}	0,8704	0,8728	0,8689	0,8727	0,8677
Iodine number	0,3	0	0	0,3	0
Fraction 167-172°					
Yield, wt. %	30,74	26,59	23,00	12,76	35,21
n_D^{20}	1,5052	1,5058	1,5051	1,5055	1,5035
d_4^{20}	0,8769	0,8761	0,8755	0,8754	0,8753
Iodine number	0,2	0	0	0,8	0
Fraction 172-180°					
Yield, wt. %	2,88	4,09	3,40	2,79	3,16
n_D^{20}	1,5105	1,5092	1,5119	1,5073	1,5103
d_4^{20}	0,8868	0,8820	0,8881	—	0,8872
Iodine number	0	0	4,1	—	—
Residue					
Yield, wt. %	24,05	23,47	20,72	22,61	24,98
n_D^{20}	1,5175	—	1,5233	1,5134	1,5174
d_4^{20}	0,8960	0,9014	0,9032	0,9006	—
Iodine number	0,2	1,8	5,5	1,5	0
Sulfonability, vol. %	100	100	100	100	100

In the course of the process a certain amount of mesitylene isomerized with formation of pseudocumene and partially of semimellitene



Besides the conversions indicated, hydrocracking of alkylbenzenes with formation of a certain amount of toluene, methane and its homologs occurred to a comparatively small extent.

SUMMARY

1. Catalytic conversion of mesitylene mixed with benzene was studied. Under conditions of an elevated pressure of 10-15 atm. and a temperature of 480°, dealkylation of mesitylene and associated alkylation of benzene occurs mainly, with formation of 18-22% toluene and ~ 17% xylenes.
2. As a result of single-stage treatment of a mixture of mesitylene and toluene over an aluminosilicate, 30-32% of a xylene fraction is formed, consisting of 45-50% m-xylene, ~ 20-25% p-xylene, and ~ 30% o-xylene. Presence of toluene and benzene depresses mesitylene isomerization practically entirely.
3. On catalytic treatment of mesitylene in presence of aluminosilicates, disproportionation of methyl groups occurs mainly, with formation of xylenes and tetramethylbenzenes. In this case, partial hydrocracking of mesitylene methyl groups occurs, with formation of a small amount of toluene, methane and its homologs.

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INVESTIGATION OF THE INFLUENCE OF THE PRESSURE, THE TEMPERATURE,
AND THE CONCENTRATION OF THIOPHENE ON THE DEGREE OF DEHYDRO-
GENATION AND ISOMERIZATION OF CYCLOHEXANE IN THE PRESENCE
OF PLATINUM CATALYSTS

Kh. M. Minachev and D. A. Kondrat'ev

The N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR.

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When studying the composition of the liquid catalyzates obtained in the investigation of the influence of thiophene on the activity of Pt-Al₂O₃ catalysts by the method of gas-liquid chromatography [1], we came across an extremely interesting fact. It was found that, on passing a mixture of cyclohexane and thiophene over platinum-alumina catalysts under reforming conditions, the catalyzates contained, in addition to the main product - benzene - and unchanged cyclohexane, considerable amounts of methylcyclopentane. Where pure cyclohexane was used, the content of methylcyclopentane in the catalyzates was far lower.

In the present work, we have investigated the influence of various factors on the degree of dehydrogenation and isomerization of cyclohexane to benzene and methylcyclopentane under reforming conditions over platinum-alumina catalysts. In pursuit of this aim, we studied the dependence of the yields of benzene and methylcyclopentane on variations in the following parameters: 1) the concentration of platinum in the catalysts, 2) the temperature, 3) the pressure, and 4) the period of working of a catalyst with a mixture of cyclohexane and thiophene. All experiments were carried out both with pure cyclohexane and with mixtures of cyclohexane and thiophene. The influence of the concentration of the thiophene in mixtures of it with cyclohexane on the degree of dehydrogenation and isomerization of the latter was also studied.

EXPERIMENTAL

Six samples of catalysts containing 0.5, 1.0, 3.0, 5.0, 7.0, and 10.0% of platinum on alumina were prepared for the investigation. The catalysts were made by impregnating tablets of the carrier, previously ignited at 500°, with chloroplatinic acid, with subsequent reduction in a current of hydrogen at 320-330° for 10-12 hours.

All experiments were carried out in an apparatus of the continuous type at 450-500° and pressures of 20-60 atm. The total velocity of feed of the initial material was 2 hours⁻¹ and the molar ratio of H₂ to hydrocarbon was 5:1. The length of experiments on fresh catalysts with pure cyclohexane was 5 hours. Experiments with mixtures of cyclohexane and thiophene lasted for 10 hours, after which the catalysts were regenerated with pure cyclohexane under the same conditions for 5 hours. Experiments with pure cyclohexane on regenerated catalysts lasted 5-10 hrs. The duration of the experiments was selected on the basis of our previous work [2, 3], in which it was shown that not more than 4-5 hours was needed to achieve stable working with a fresh catalyst and that in the presence of thiophene the activity of the catalysts underwent practically no further change after 2-3 hours working. In addition, it was found that complete regeneration of the dehydrogenation activity of Pt-Al₂O₃ catalysts took place after 5 hours' working with pure cyclohexane. The liquid products of catalysis, without previous debutanization, were analysed by gas-liquid chromatography [1]. The gases issuing from the apparatus were freed from hydrogen sulfide, which was recovered in the form of zinc sulfide. The experimental results obtained are given in Tables 1 and 2 and in Figures 1-3.

It follows from the figures given in Column 3 of Table 1 that when the concentration of platinum in the catalysts is increased from 0.5 to 1% the degree of conversion of pure cyclohexane to benzene increases by 9%, while a further change in the concentration of platinum up to 10% increases the dehydrogenation capacity of the catalyst

TABLE 1. Dehydrogenation of Pure Cyclohexane and Mixtures of it with 1% of Thiophene at 450° Over Catalysts with Varying Contents of Platinum. (pressure 20 atm.; $v = 2 \text{ hr}^{-1}$; and $\text{H}_2 : \text{HC} = 5 : 1$)

Catalysts	Reaction products	Composition of the catalyzate, % by weight		
		Pure cyclohexane on fresh catalysts	Mixture of cyclohexane and 1% of thiophene	Pure cyclohexane on re-generated catalysts
1	2	3	4	5
Al_2O_3 (pure)	Benzene	0.6	0.5	—
	Methylcyclopentane	1.7	1.7	—
	Cyclohexane	97.7	97.8	—
	$\text{C}_5 - \text{C}_6$ Alkanes + gas	traces	traces	—
0.5% $\text{Pt} - \text{Al}_2\text{O}_3$	Benzene	72.9	16.8	69.9
	Methylcyclopentane	12.9	22.6	10.0
	Cyclohexane	14.2	60.3	20.1
	$\text{C}_5 - \text{C}_6$ Alkanes + gas	traces	traces	traces
1.0% $\text{Pt} - \text{Al}_2\text{O}_3$	Benzene	81.1	42.9	82.0
	Methylcyclopentane	7.7	23.1	5.0
	Cyclohexane	9.4	34.0	13.0
	$\text{C}_5 - \text{C}_6$ Alkanes + gas	1.8	traces	traces
3.0% $\text{Pt} - \text{Al}_2\text{O}_3$	Benzene	82.9	53.0	82.1
	Methylcyclopentane	7.6	16.3	5.5
	Cyclohexane	7.5	30.5	12.4
	$\text{C}_5 - \text{C}_6$ Alkanes + gas	2.0	0.2	traces
5.0% $\text{Pt} - \text{Al}_2\text{O}_3$	Benzene	84.3	65.4	84.8
	Methylcyclopentane	7.4	8.5	5.8
	Cyclohexane	6.2	26.0	8.5
	$\text{C}_5 - \text{C}_6$ Alkanes + gas	2.1	0.1	0.9
7.0% $\text{Pt} - \text{Al}_2\text{O}_3$	Benzene	85.8	68.2	85.5
	Methylcyclopentane	4.5	6.6	3.7
	Cyclohexane	9.0	25.0	10.8
	$\text{C}_5 - \text{C}_6$ Alkanes + gas	0.7	0.2	traces
10.0% $\text{Pt} - \text{Al}_2\text{O}_3$	Benzene	89.3	72.3	89.7
	Methylcyclopentane	3.7	4.6	2.5
	Cyclohexane	7.0	23.1	7.8
	$\text{C} - \text{C}$ Alkanes + gas	traces	traces	traces

by only 8%. These figures agree with the results obtained by Hettinger et al [4] on the dehydrogenation of methylcyclohexane on catalysts containing 0.25, 0.35, 0.60 and 1.0% of platinum on alumina. Thus, the fact [4, 5] that the activity of a catalyst does not change proportionally to an increase or decrease of the content of metal in it is once again confirmed.

With an increase in the concentration of platinum in the catalyzate, the content of methylcyclopentane in the catalyzates gradually diminishes, being 3.7 and 4.5% at 10.0 and 7.0% of platinum, respectively, and almost 13% at 0.5% of platinum.

When cyclohexane containing 1% of thiophene is converted on the same catalysts under the same conditions, a somewhat different picture is observed in the ratio of the reaction products (see Column 4 of Table 1). The content of benzene in all the catalyzates is considerably less than in the case of the action of the same catalysts on pure cyclohexane. However, the content of methylcyclopentane in all catalyzates obtained in the presence of thiophene is higher than in the catalyzates of pure cyclohexane. Thus, on the 0.5% and 1.0% catalysts, about 23% of methylcyclopentane is formed. The variations in the content of benzene and methylcyclopentane in the catalyzates with time and in dependence on the concentration of platinum in the catalyst are shown in Figs. 1 and 2. As can be seen from these curves, at the same concentration of thiophene in the initial cyclohexane, the yields of benzene and methylcyclopentane over all catalysts change markedly in the course of the first few hours working, after which they

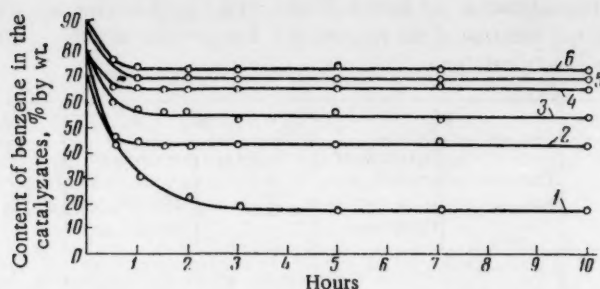


Fig. 1. Variation in the content of benzene in the catalyzates on working with Pt-Al₂O₃ catalysts for 10 hours with a mixture of cyclohexane and 1% of thiophene (450°, 20 atm.): 1 - 0.5% Pt; 2 - 1% Pt; 3 - 3% Pt; 4 - 5% Pt; 5 - 7% Pt; 6 - 10% Pt

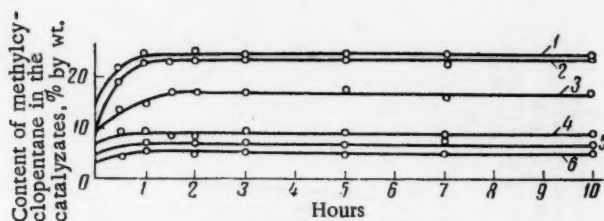


Fig. 2. Variation in the content of methylcyclopentane in the catalyzates on working with Pt-Al₂O₃ catalysts for 10 hours with a mixture of cyclohexane and 1% of thiophene (450°, 20 atm.): 1 - 0.5% Pt; 2 - 1% Pt; 3 - 3% Pt; 4 - 5% Pt; 5 - 7% Pt; 6 - 10% Pt

become stabilized at a definite level which depends on the concentration of platinum in the catalyst. It must be noted that as the content of platinum in the catalyst increases the influence of the poison on the yields of benzene and methylcyclopentane diminishes.

In a manner similar to that which was demonstrated in our previous investigations [2, 3, 6], the deactivated catalysts are completely restored to their initial dehydrogenation activity (see Column 5 of Table 1) on passing pure cyclohexane over them under the experimental conditions. However, the isomerization capacity of the regenerated catalysts is somewhat lower as compared with fresh catalysts.

Figure 3 shows the variation in the content of the components in the reaction products obtained on a 1% Pt-Al₂O₃ catalyst at various temperatures and a pressure of 20 atm. as a function of the concentration of thiophene in the initial cyclohexane. As can be seen from the curves, with an increase in the concentration of thiophene from 1 to 3%, the degree of isomerization of the cyclohexane into methylcyclopentane at 450° rises from 23.1 to 32.5%. Side by side with this, the yield of benzene falls from 43 to 11.8%. A further increase in the concentration of thiophene by a factor of two (from 3 to 6%) has practically no influence on the yield of methylcyclopentane, while the content of benzene in the catalyzates continues to decrease and reaches 6.4%. On carrying out the same process at a temperature of 500°, the yield of methylcyclopentane continuously rises with an increase in the concentration of thiophene and at 6% it finally reaches 47.5%. Simultaneously, the yields of benzene change in the opposite way to the yields of methylcyclopentane and reach 13.5%. In addition, special experiments were carried out which showed that at a temperature of 400° and a pressure of 20 atm. the addition of 1% of thiophene to the initial cyclohexane almost completely suppressed dehydrogenation (yield of benzene - 3.4%) and slightly increased the isomerization of the cyclohexane (yield of methylcyclopentane - 8.3%) on a 1% Pt-Al₂O₃ catalyst.

The results of experiments on the conversion of pure cyclohexane and a mixture of it with 6% of thiophene at 500° and various pressures on a 1% platinum-alumina catalyst are summarized in Table 2.

It can be seen from the figures of Table 2 that, in the case of the conversion of pure cyclohexane, on raising the pressure from 20 to 60 atm. the content of methylcyclopentane in the catalyzates increases corresponding from

TABLE 2. Degree of Hydrogenation and Isomerization of Pure Cyclohexane and a Mixture of it with 6% of Thiophene as a Function of the Pressure at a Temperature of 500°. ($v = 2 \text{ hr}^{-1}$ and $\text{H}_2 : \text{HC} = 5 : 1$ on a 1% Pt - Al_2O_3 catalyst)

Pressure, atm.	20		40		60	
Starting material	Pure cyclohexane	Mixture of cyclohexane with 6% of thiophene	Pure cyclohexane	Mixture of cyclohexane with 6% of thiophene	Pure cyclohexane	Mixture of cyclohexane with 6% of thiophene
Reaction products	Composition of the catalyzates, % by weight.					
Benzene	86.5	13.5	65.4	9.3	38.8	10.5
Methylcyclopentane .	7.7	47.5	19.8	57.0	37.3	56.1
Cyclohexane	3.6	34.0	5.9	27.2	7.1	26.5
$\text{C}_5 - \text{C}_6$ Alkanes + gas	2.2	5.0	8.9	6.5	16.8	6.9

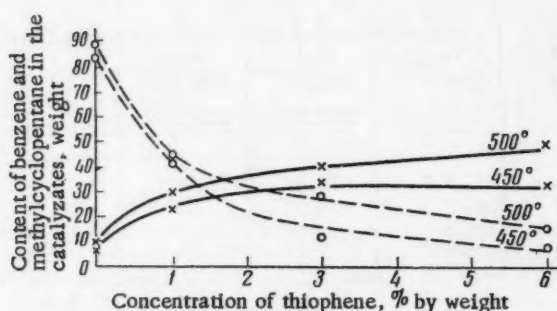


Fig. 3. Variation in the yields of methylcyclopentane (continuous lines) and benzene (broken lines) as a function of the concentration of thiophene in the cyclohexane at 450 and 500° (pressure 20 atm.)

7.7 to 37.3%. A completely different picture is observed in the conversion of the mixture of cyclohexane and thiophene. Thus, the content of methylcyclopentane in the catalyzate obtained at 20 atm. is 47.5%, while on carrying out the experiment under a pressure of 40 atm. the catalyzate contained 57% of methylcyclopentane; a further increase in the pressure to 60 atm. did not give rise to any change in the yields of methylcyclopentane. Thus, the greatest yield of methylcyclopentane from cyclohexane may be obtained by passing cyclohexane containing 6% of thiophene at 40 atm. and 500°.

It must be noted that, in addition to benzene, methylcyclopentane and cyclohexane, all the catalyzates contained a certain amount of, mainly, n-hexane, 2- and 3-methylpentane and 2, 2- and 2, 3-dimethylbutanes, which are formed as a result of the hydrogenolysis of the cycloalkanes, and also a small amount of pentane, isopentane and dissolved $\text{C}_1 - \text{C}_4$ gaseous hydrocarbons, the presence of which is explained by hydrocracking taking place during the process. It was found that neither an increase in the concentration of platinum in the catalyst nor variation of the temperature at any one pressure exerted an essential influence on the formation of these products from pure cyclohexane. However, as can be seen from Table 2, in experiments with pure cyclohexane at 500°, with a rise in the pressure from 20 to 60 atm., the content of alkanes in the catalyzates rose sharply from 2.2 to 16.8%, the bulk of them in this case being hexane and 2- and 3-methylpentanes. On adding a certain amount of thiophene to the initial hydrocarbon, the yield of butane increased correspondingly at the expense of the hydrogenolysis of the latter, while the content of other alkanes in the catalyzate at 40 and 60 atm. not only did not increase but even decreased appreciably in comparison with experiments without the addition of thiophene (see Table 2). These results indicate that the assertion of Hettinger et al [4] that hydrocracking increases in the presence of sulfur compounds holds good only for pressures of the order of 20 atm. At higher pressures (40 and 60 atm.) no increase in hydrocracking in the presence of thiophene was observed.

Thus, it follows from the experimental results presented, that an increase in the pressure, a diminution in the temperature, a diminution in the concentration of platinum, or the introduction of thiophene into the reaction zone under reforming conditions leads to a decrease in the degree of dehydrogenation of cyclohexane and simultaneously to an increase in the degree of its isomerization. The inverse variation of the yields of benzene and methylcyclopentane could be explained by an increase in the concentration of unchanged cyclohexane and, therefore, an increase in the velocity of its isomerization.

SUMMARY

1. The conversions of pure cyclohexane and mixtures of it with varying amounts of thiophene have been studied under reforming conditions at 400–500° and 20–60 atm. on fresh, deactivated, and regenerated catalysts containing 0.5–10.0% of platinum on alumina.
2. On changing the temperature of the experiment from 400 to 500° while passing a mixture of cyclohexane with 1% of thiophene over a 1% Pt–Al₂O₃ catalyst, the content of methylcyclopentane in the catalyzates rises correspondingly from 8.3 to 29%, and the content of benzene increases from 3.4 to 42.1%.
3. Raising the pressure of the experiment from 20 to 60 atm. promotes an increase in the yield of methylcyclopentane both from pure cyclohexane and in the presence of thiophene. Thus, in the conversion of pure cyclohexane at 40 atm. and 500°, the catalyzate contains 37.3% of methylcyclopentane and 65.4% of benzene, while in the presence of 6% of thiophene the yields of methylcyclopentane and benzene under the same conditions are 57 and 9.3%, respectively.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. *Some or all of this periodical literature may well be available in English translation.* A complete list of the cover-to-cover English translations appears at the back of this issue.

FREE-RADICAL ADDITION OF PRIMARY ALCOHOLS TO α -OLEFINS

G. I. Nikishin, V. D. Vorob'ev and A. D. Petrov

The N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR

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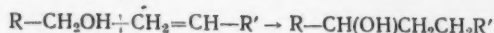
Nauk, 1961, No. 5,

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The synthesis of individual secondary alcohols in laboratory practice is generally carried out by two methods — the reduction of ketones and the Grignard reaction. These methods are quite simple in experimental formulation; however, when they are applied to the synthesis of higher alcohols, a series of lengthy operations is involved in the preparation of the initial aldehydes and ketones. Urry et al showed that secondary alcohols are readily obtained in one step by the addition of primary alcohols (ethanol and butanol) to α -olefins (hexene and octene). The reaction proceeds by a radical chain mechanism initiated by *t*-butyl peroxide or ultraviolet light. Secondary alcohols (propan-2-ol, butan-2-ol and cyclohexanol) add to olefins with the formation of tertiary alcohols [1]. However, with none of the alcohols mentioned could a high yield of the 1 : 1 adduct be obtained. Thus, at a reaction temperature of 117–118° and a molar ratio of butan-1-ol : oct-1-ene : peroxide of 32.5 : 1 : 0.8, the yield of dodecan-4-ol was 37.3 %; at a reaction temperature of 115–118° and a molar ratio of ethanol : oct-1-ene : peroxide of 25.2 : 1 : 0.1, the yield of dodecan-2-ol was 23.9%. Another fundamental disadvantage of this method consists in the fact that long periods of heating the reaction mixture (~ 40 hours) are required for carrying out the reaction. The whole of the calculated quantity of peroxide was introduced into the solution of olefin and alcohol before the start of the experiment.

In the present work, the synthesis of C_{13} – C_{18} secondary alcohols was carried out by the free-radical addition of normal primary alcohols to normal α -olefins.



The work was undertaken for the purpose of studying monomolecular films of alcohols on water further, and also for the purpose of studying the surface-active properties of the sodium salts of the sulfated alcohols. We set ourselves the task of elucidating the influence of the reaction conditions, the method of carrying out the experiment, and the ratio of the components and the peroxide on the yield of the 1 : 1 adduct.

TABLE 1

Experiment No.	Reaction Components		Amounts used in the reaction, M			Temperature, °C	Time hours	Yield of 1 : 1 adduct		Residue, g
	alcohol	olefin	alcohol	olefin	peroxide				%*	
1	Pentan-1-ol	Dec-1-ene	3	0,15	0,075	134–135	3	9	26,6	13,8
2	Pentan-1-ol	Tridec-1-ene	3	0,15	0,045	133–136	6	8,3	20,5	13,5
3	Hexan-1-ol	Oct-1-ene	3	0,18	0,045	144–148	6,5	16,2	42,2	14
4	Hexan-1-ol	Dec-1-ene	3	0,15	0,075	150–156	3	19	52,2	14,3
5	Heptan-1-ol	Hex-1-ene	2,6	0,23	0,041	155–168	7	14	30,8	12
6	Heptan-1-ol	Hept-1-ene	3	0,15	0,045	164–171	6	17,2	53	12,3
7	Octan-1-ol	Hept-1-ene	3	0,15	0,045	180–186	4	16,2	17,3	14,5
8	Octan-1-ol	Non-1-ene	3	0,15	0,075	160–170	3	23,4	60,8	12,3
9	Nonan-1-ol	Hex-1-ene	3	0,15	0,045	200–210	6	17,5	51	6,6
10	Nonan-1-ol	Oct-1-ene	3	0,15	0,045	195–202	7	24,3	63,2	13,7
11	Decan-1-ol	Hex-1-ene	3	0,15	0,045	180–195	6	19,2	52,2	—
12	Decan-1-ol	Hept-1-ene	3	0,15	0,075	180–200	5	25	65	14,7
13	Heptan-1-ol	Dec-1-ene	3	0,15	0,025	165–170	3	2	5,2	5,8

*Calculated on the olefin taken.

TABLE 2

Experiment No.	1:1 adduct	Melting point, °C		Found, %		Calculated, %	
		determined by us	Literature data [2]	C	H	C	H
1	C ₄ H ₉ CH(OH)—C ₁₀ H ₂₁	35,8—36,2(2)*	37,5—37,8(4)	78,84 79,03	14,22 14,24	78,87	14,12
2	C ₄ H ₉ CH(OH)—C ₁₃ H ₂₇	47,5—48,5(2)	48,6—50,3(5)	80,20 80,07	13,90 14,11	79,92	14,16
3	C ₈ H ₁₁ CH(OH)—C ₈ H ₁₇	30 —30,5(6)	32 —34(8)	78,25 78,18	13,94 14,15	78,43	14,10
4	C ₈ H ₁₁ CH(OH)—C ₁₀ H ₂₁	40,5—41(2)	41,7—42,9(9)	79,33 79,45	13,77 13,86	79,26	14,13
5	C ₈ H ₁₃ CH(OH)—C ₈ H ₁₃	41,5(2)	43[3]	77,85 77,99	13,89 13,84	77,93	14,09
6	C ₈ H ₁₃ CH(OH)—C ₇ H ₁₅	42,2—42,5(2)	43 —44(6)	78,62 78,46	13,95 14,02	78,43	14,10
7	C ₇ H ₁₅ CH(OH)—C ₇ H ₁₅	50,5—51(2)	52 —52,6(3)	78,35 78,58	13,80 13,81	78,87	14,12
8	C ₇ H ₁₅ CH(OH)—C ₉ H ₁₉	51 —51,6(4)	52,2—53(5)	79,80 79,93	14,01 14,09	79,61	14,14
9	C ₈ H ₁₇ CH(OH)—C ₈ H ₁₃	41 —42(4)	43 —44(9)	78,70 78,66	14,13 14,16	78,87	14,12
10	C ₈ H ₁₇ CH(OH)—C ₈ H ₁₇	59,5—60(2)	60,8—61,2(8)	79,95 79,88	14,04 14,13	79,61	14,14
11	C ₉ H ₁₉ CH(OH)—C ₈ H ₁₃	42 —42,5(5)	44,5—46(13)	78,82 78,80	14,11 13,87	79,26	14,13
12	C ₉ H ₁₉ CH(OH)—C ₇ H ₁₅	50,0—51,0(2)	52,3—53(5)	79,80 79,91	14,17 14,23	79,61	14,14
13	C ₈ H ₁₃ CH ₂ (OH)—C ₁₀ H ₂₁	46,0—46,6(2)	47,2—48,9(7)	79,83 80,01	14,10 14,26	79,61	14,14

* The number of recrystallizations is shown in brackets.

TABLE 3

Experiment No.	Amount used for the reaction, M			Temperature, °C	Time, hours	Yield		Residue
	nonyl alcohol	octene	peroxide			g	%*	
14	3	0,15	0,045	155—165	1/4	13,5	35,2	13,5
15	3	0,15	0,045	155—165	1	16,5	43,0	11,3
16	3	0,15	0,045	155—165	3	19,5	50,8	13,7
17	3	0,15	0,045	155—165	6	21,5	56,3	13,1
18	3	0,15	0,045	155—165	10	23,7	61,7	9,3
19	3	0,15	0,045	95—105	6	—	—	—
20	3	0,15	0,045	118—122	6	3,7	9,6	6,2
21	3	0,15	0,045	127—139	6	15,0	39,0	17,7
22	3	0,15	0,045	140—145	6	22,3	58,1	10,2
23	3	0,15	0,045	180—185	6	21,2	55,2	13,6
24	3	0,15	0,045	196—203	6	20,5	53,4	7,2
25	3	0,15	0,015	155—165	3	10,4	27,3	8,7
26	3	0,15	0,075	155—165	3	24,0	62,5	15
27	3	0,15	0,105	155—165	3	26,0	67,7	—
28	0,375	0,15	0,075	155—165	3	7,2	18,7	15,4
29	0,75	0,15	0,075	155—165	3	14,2	37,0	14,3
30	1,5	0,15	0,075	155—165	3	20,1	52,3	20,8
31	6	0,15	0,075	155—165	3	25,5	66,4	19,7

* Calculated on the olefin taken.

The main features of the various experiments are given in Table 1. Table 1 includes the names of the alcohols and olefins, their amounts and molar ratios, the amount of peroxide, the temperature and time of the reaction, the yield of 1 : 1 adducts, and the amount of higher-boiling residue. Table 2 gives the structures of the alcohols obtained, their melting points and the most reliable melting points found in the literature [2], and the results of elementary analysis. The fairly high boiling points of the alcohols selected by us allowed the addition reactions initiated by *t*-butyl peroxide (experiments 1-12) to be carried out under atmospheric pressure in glass apparatus. In experiments 1, 4, 5, and 8-12 a solution of the peroxide and the olefin in the alcohol was introduced into the reaction space uniformly, in drops, during the whole time of the reaction; in experiments 2, 3, 6, 7, 9, 10, and 11 the same solution was also introduced uniformly, but the concentration of peroxide and olefin in it were changed. However, this variation in procedure had no effect on the yields of the adducts. The small amounts of 1 : 1 addition products formed in experiments 1 and 2 are explained by the insufficiently high reaction temperature (boiling point of amyl alcohol, 137°). The low yield of tridecan-7-ol in experiment 5 is explained by the inadequate amount of peroxide. Experiments 1 - 12 were carried out under non-standard conditions, since we had not set ourselves the task of investigating the influence of the molecular weight of the alcohols and the olefins on the chain transfer constant and the yield of 1 : 1 adducts. Obviously, this influence is very slight in the series of compounds given in Table 1; to a large degree, the yields of products are determined by the reaction conditions, the ratio of the components and the amount of peroxide. In all the experiments, in addition to the 1 : 1 adducts, higher-boiling substances were formed among which a diol product of the recombination of R-CHOH radicals - was almost always present.

In the paper cited above [1] it was shown that benzoyl peroxide (at 80 - 140°) and 2,2'-azobisisobutyronitrile (at 80°) are incapable of initiating the addition of alcohols to olefins. It was assumed here that the R-CHOH alcohol radical formed reacts with the peroxide, forming $R-CH(OH)OCOC_6H_5$ and $C_6H_5COO^{\cdot}$. According to our results (experiment 13), the addition of alcohols to olefins under the action of benzoyl peroxide is possible at 160 - 170°; however, the adduct is obtained in low yield. With 2,2'-azobisisobutyronitrile at 160°, a 1 : 1 adduct could not be obtained. In a series of specially contrived experiments (Table 3) using the addition of nonan-1-ol to oct-1-ene as a model, the influence of the temperature and time of the experiments (time of addition of the olefin and peroxide to the alcohol : olefin : *t*-butyl peroxide on the yield of heptadecan-9-ol was studied. The experiments shown in Table 3 may be divided into four groups. In each group, one of the characteristics of the reaction is changed and three remain constant.

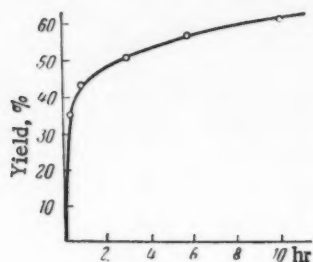


Fig. 1

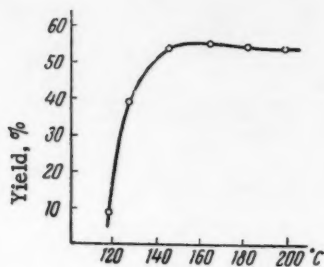


Fig. 2

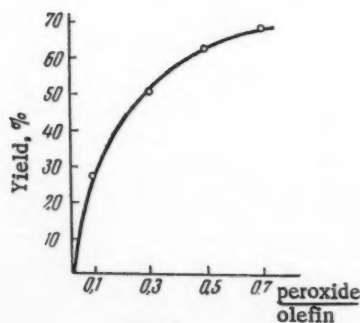


Fig. 3

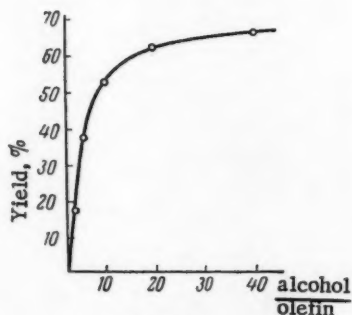


Fig. 4

Experiments 14-18 were carried out at a temperature of 155-165° and with a constant alcohol : olefin : peroxide ratio of 20 : 1 : 0.3. The variable magnitude was the time of the reaction. As can be seen from Table 3, after 15 minutes heptadecan-9-ol was obtained with a yield of 35% and the yield rises considerably with an increase in the time of reaction to three hours, when it is 50.8% (Fig. 1), and it increases further to a smaller extent at 6 and 10 hrs. Consequently, it is not necessary to increase the reaction time to 40 hours, as was done earlier [1]. The influence of the temperature is displayed even more clearly (experiments 17, 19-24). The reaction does not go at 100°; at 118-122°, i.e. in the temperature range in which Urry worked, it takes place very slowly. Only part of the olefin is consumed and pentadecan-9-ol is obtained in very low yield - 9.6%. The yield rises sharply at 140-145° (Fig. 2) and then remains practically constant with an increase in the temperature to 200°. The amount of peroxide used increases the yield of 1 : 1 adduct proportionally (experiments 14, 25-27). The greatest increase in yield (23.5%) is found when the amount of peroxide is increased from 0.1 to 0.3 moles, calculated on the olefin taken (Fig. 3); a further increase in the amount of peroxide to 0.5 and 0.7 moles gives a smaller increase in the yield (12 and 5%, respectively). The optimum ratio of alcohol to olefin is 10 : 1 - 20 : 1 (experiments 26, 28-31). Increasing the ratio to 40 : 1 does not greatly increase the yield, while decreasing the ratio reduces it markedly (Fig. 4). In order to evaluate the influence of the temperature on the chain transfer constant *C* approximately, we compared experiments 20 and 23, which were carried out at 120 and 180°, respectively. The diol was distilled off from the residues obtained in these experiments and it was assumed, somewhat arbitrarily, that the residue consisted of a mixture of telomer-homologs. In experiment 20, the amount of 1 : 1 adduct was 44% and the amount of telomer-homologs 56%, their mean molecular weight being 501. In experiment 23, the 1 : 1 adduct amounted to 71% and the telomer-homologs to 29%, their mean molecular weight being 440. On calculating the chain transfer constant from these figures [1] the following values were obtained: at 120°, *C* = - 0.4; at 180°, *C* = - 0.1.

EXPERIMENTAL

All experiments shown in Tables 1 and 3, with the exclusion of 13, were carried out by a single procedure. In experiments 1, 4, 5, 8, 12, and 14-31, a solution of *t*-butyl peroxide and the olefin in 30 g of the alcohol taken from the total calculated amount of alcohol shown in the tables was prepared. The solution was added uniformly, in drops, to the alcohol placed in the flask and heated to the required temperature. In experiments 2, 3, 6, 7, and 9-11, three solutions were prepared: a) half the total amount of olefin, 1.5 g of peroxide and 10 g of alcohol; b) the other half of the olefin, 3.5 g of peroxide and 10 g of alcohol; and c) 1.5 g of peroxide and 10 g of alcohol. Solutions (a) (b) (c) were introduced successively into the reaction vessel: (a) and (b) over the time shown in Table 1 less 45-60 min.; in the remaining 45-60 min., solution (c) was added. All the experiments were carried out with stirring. After the completion of the addition of the solution, the reaction mixture was heated for an additional hour; then low-boiling substances (acetone, *t*-butyl alcohol, olefin) and the excess of alcohol were distilled off from it. The secondary alcohol - the 1 : 1 adduct - was distilled off in vacuo from the high-boiling product obtained, after which the diol and products of telomerization remained in the flask. The sum of these amounts is shown in Tables 1 and 3 in the column "Residue". The secondary alcohols obtained were recrystallized from acetone, after which their melting points were determined in a capillary placed in a block. In experiment 10, when the residue was distilled ~ 2 g of a substance boiling at 180-200° (2 mm) was obtained. After two recrystallizations from acetone, octadecan-9, 10-diol with m.p. 128.5-129° was obtained from this fraction. Found: C 75.49, 75.38; H 13.12, 13.11%. $C_{18}H_{38}O_2$. Calculated: C 75.46; H 13.36%. In experiment 13, a solution of 21 g of decene in 30 g of heptanol was added to 318 g of heptanol uniformly in drops, and the peroxide was added in six portions of one gram each after approximately equal intervals of time.

SUMMARY

1. The synthesis of a series of secondary alcohols has been carried out by the addition of C_5 - C_{10} primary alcohols to C_6 - C_{13} α -olefins. The reaction initiator was *t*-butyl peroxide.
2. The optimum conditions for this reaction are: temperature, 140-160°; time, 3-6 hours; molar ratio alcohol : olefin : peroxide = 20 : 1 : 0.3.

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PRODUCTS OF THE NITRATION OF α - AND α' -AMINONICOTINES

Ya. L. Gol'dfarb, L. V. Antik and V. A. Petukhov

The N. D. Zelinskii Institute of Organic Chemistry of the Academy of Sciences of the USSR

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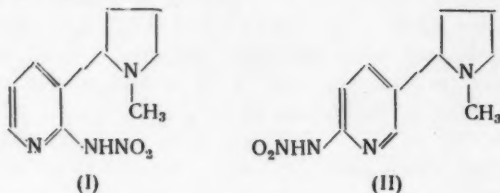
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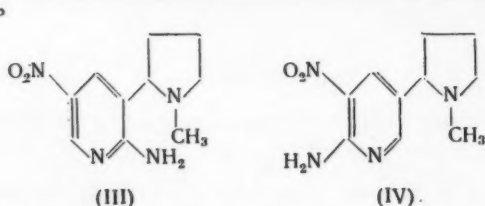
As early as 1915, Chichibabin and Razorenov found that the action of nitric acid on α -aminopyridine in concentrated sulfuric acid at a low temperature led to the formation of the product substituted in the amino group - α -nitraminopyridine*. Later, analogous compounds were obtained from homologs and derivatives of this amine [2], from β -aminopyridine [3] and γ -aminopyridine [4], and from amino derivatives of other heterocyclic systems, for example 2-aminothiazole [5] and α -aminoanabasine [6] which stands close the nicotine derivatives considered here.

Gol'dfarb and Popov initiated the study of the nitration of α -aminonicotine in our laboratory in 1936, but this work was soon interrupted and has only recently been resumed by us. At the present time, we are able to communicate some results relating to the nature, and to a series of interesting properties, of the α - and α' -nitraminonicotines formed from the corresponding aminonicotines under the conditions for obtaining α -nitraminopyridine. That is, by the action of nitric acid in concentrated sulfuric acid with cooling on α - and α' -aminonicotines compounds are formed having the composition corresponding to formulas (I) and (II)



which preserve the pyrrolidine ring, as is confirmed by the production from them (see below) of the corresponding hydroxynicotines earlier described by Chichibabin and Kirsanov [7].

α - and α' -Nitraminonicotines possess acidic properties and give potassium and sodium salts with concentrated solutions of caustic alkalis; they are stable in an acid medium at low temperatures, but on heating with concentrated sulfuric acid they change in two directions: mainly to α - (or α' -) hydroxynicotines with the liberation of N_2O and, to a smaller extent, to α - (or α' -) amino- β' -nitronicotines (III) or (IV). These aminonitro derivatives may be obtained, though in smaller yields, without isolating the intermediate nitraminonicotines.

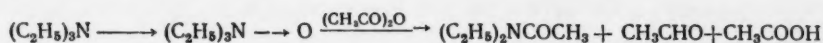


Thus, to a certain extent (I) and (II) repeat the properties of α -nitraminopyridine; however, on studying the gases formed as a result of the action of acetic anhydride diluted with acetic acid on the nitramines mentioned an

* We preserve the name α -nitraminopyridine for this compound, regardless what forms of amino-imino tautomerism predominate in actual cases.

essential difference between the behaviour of nitramines (I) and (II) and that of nitraminopyridine is observed: while the latter under these conditions gives nitrous oxide, (I) and (II) form a mixture of gases containing 80 - 90% of nitrogen. It may be assumed that this difference is connected with the presence in the molecules of (I) and (II) of an N-methylpyrrolidine ring capable of being oxidized at the expense of the nitramino group - for example, with the formation of N-oxides decomposing to nor-bases under the action of acetic anhydride; a similar conversion of N-oxides, in particular N-oxides of nicotine, has been observed by the Polonovskis [8].

In view of this, it was of interest to follow the decomposition of α -nitraminopyridine under the action of acetic anhydride in the presence of an equimolecular amount of an aliphatic tertiary amine, which should be in the relationship mentioned and capable of playing the role of the N-methylpyrrolidine ring of the nitraminonicotines. Experiments with the participation of triethylamine and N-methylpiperidine, as could be assumed, went with the formation of a gas consisting almost entirely (~ 90%) of nitrogen. For the reaction with triethylamine, we were able to show the presence in the mixture of diethylacetamide, which might be formed in accordance with the scheme

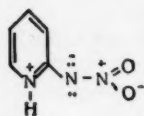


However, the yield of diethylacetamide (12 - 25%) was far from corresponding to the yield of nitrogen (70 - 80%). Apparently other products of the oxidation or decomposition are contained in the resinified part of the material *.

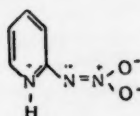
The formation of nitrogen in the decomposition of nitraminonicotines is not typical for the decomposition of nitramines. There is a description in the literature of an example of the decomposition of some nitramines of the general formula $\text{RR}^1\text{CHNHNO}_2$ [9] on heating in alkaline solution, which leads to the formation of a ketone and the liberation of nitrogen, but the authors show that, apparently, a very strong requirement for such decomposition is the presence of an atom of hydrogen on the α -carbon atom. With acid catalysis, the decomposition of primary aliphatic nitramines generally takes place with the liberation of N_2O and the formation of an alcohol (or an alkyl halide or an olefin), see, for example, [10]. Under the influence of acids, primary aromatic nitramines mainly isomerize into the corresponding C-nitroanilines, see, for example [11].

Reference must also be made to the data given in the literature which characterize the relatively easy reduction of aromatic nitramines but do not, however, give a clear explanation of this reaction since accurate information on the nature of the oxidation products formed is lacking. This is the case with the reduction of certain secondary aromatic nitramines to nitrosamines reported by Reverdin in a series of papers [12], or the formation of diazo compounds on the isomerization of aromatic nitramines reported by Bamberger [13] or, on the other hand, by Bradfield and Orton [14].

The results of the experiments reported impelled us to study the decomposition of nitraminonicotines in concentrated sulfuric acid more closely by investigating the composition of the gas formed; under these conditions the specific influence of the tertiary amine (pyrrolidine) part of the molecule is excluded and nitramines (I) and (II) must decompose in the same direction as 2-nitraminopyridine, i.e. with the formation of nitrous oxide. This was confirmed completely by the experiment: nitrous oxide, containing only ~ 6 - 10% of nitrogen, was obtained from both isomers. At the present time, knowledge of the structure of nitramines is still inadequate to explain the nature of their decomposition under various conditions. Sheinker studied the infrared and ultraviolet spectra of α -nitraminopyridine [15]. From these, this author concluded that, in the crystalline state and in aqueous and alcoholic solution, this compound had the imino structure, while in dioxane solution a considerable content of the amine of the tautomeric form was observed. Taurins [16], on the basis of a study of the infrared spectrum of α -nitraminopyridine, assigned to it, in the solid state, the structure of an internal salt - nitrimino- (1H)-pyridinium betaine and treated it as a resonance hybrid with the predominating structures



and



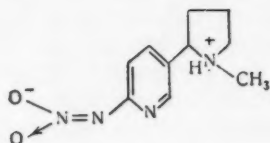
* It must be assumed that the oxidizing properties are inherent in the nitramino group as such, and not in the nitrous oxide formed, which has no oxidizing action on the tertiary amine (see experimental part).

For comparison we may refer to the work of Salyamon and Bobovich [17] and Salyamon, Gracheva and Porai-Koshitsa [18], in which the authors came to the conclusion from the data of potentiometric analysis, in conformity with the Raman spectra, that aromatic nitramines exist in solution in two forms: in alkaline solution, as salts of the acid $RNHNO_2$; and in acid solution, as the oxidiazohydroxides $RN = NOOH$.

In view of this inadequacy of the data, it seemed desirable, apart from the question of the actual structure of the nitramines in solution, to ascertain whether a parallelism exists between the chemical behaviour of the nitramines under consideration and their state in various media, which can be characterized by their ultra-violet absorption spectra to a known degree.

The Table gives λ_{\max} and ϵ_{\max} for the absorption spectra of α -nitraminopyridine and its nicotine analogs in various media and in admixture with triethylamine *. In spite of the fact that, in a number of cases, broad absorption bands with obscurely expressed peaks were observed, it is possible to make the following assertions:

1. The absorption curves of the nitramines under consideration depend on the pH of the medium: in an acid medium the absorption maximum is displaced to the long wavelength region; in an alkaline medium, in the direction of shorter wavelengths.
2. Although the absorption curves of the nitraminonictines, on replacing one medium by another, are displaced in the same direction as in the case of α -nitraminopyridine, the question of their tautomerism remains open since, in contrast to nitraminopyridine, they may exist in neutral media (for example, in alcohol) in the form of internal salts, for example:



TABLE

Solvent	α -nitraminopyridine		α -nitraminonictine		α -nitraminonictine	
	$\lambda_{\max}, m\mu$	ϵ_{\max}	$\lambda_{\max}, m\mu$	ϵ_{\max}	$\lambda_{\max}, m\mu$	ϵ_{\max}
0.1 N solution of HCl in ethanol	345	(16 800)	348	(12 000)	345	(17 300)
	272	(8000)	282	(9900)	280	(10 500)
Glacial acetic acid			348	(10 900)	345	(16 400)
			280	(11 400)	279	(10 000)
Glacial acetic acid + triethylamine *	339	(8000)				
	270	(6600)				
Ethanol	344	(15 700)	345	(14 200)	320	(6800)
	272	(8200)	274	(10 400)	276	(8800)
Ethanol + triethylamine	342	(9350)***				
	273	(7300)				
	310	(8000)****				
	276	(7600)				
0.1 N solution of NaOH in ethanol					268	(7400)
	302	(14 000)	308	(14 000)	240	(8000)

* Molar ratio of nitraminopyridine to triethylamine = 1 : 10 at a concentration of the nitramine $c = 0.000044$.

** Molar ratio of nitraminopyridine to triethylamine = 1 : 1.

*** $c = 0.000022$ M.

**** $c = 0.0001$ M.

* The spectra were obtained on the SF-4 spectrophotometer.

3. In an acid medium (0.1 N solution of HCl in ethanol) the picture of the absorption of all three nitramino derivatives is almost identical. This may be explained by the fact that, under such conditions, any interaction of the nitramino group with the pyrrolidine nitrogen atom is excluded since the formation of an ammonium salt takes place with the proton of the mineral acid. Thus, the formation of nitrous oxide in sulfuric acid solutions of the three nitramines considered agrees with the similarity of their absorption in an acid medium.

4. The absorption curves for nitraminopyridine and α' -nitraminonicotine in: a) neutral (ethanol) and b) alkaline (0.1 N NaOH in alcohol) media are extremely close.

5. α -Nitraminonicotine (I), according to the nature of its absorption in a neutral, and to an even greater degree, in an alkaline medium, differs from its isomer (II). This, most probably, is connected with the proximity in space of the nitramino group to the pyrrolidine nitrogen atom in the α -isomer.

6. The behaviour of α -nitraminopyridine in alcoholic solution in the presence of an equimolecular amount of triethylamine differs according to the concentration of the solution. The absorption spectrum of the less concentrated solution ($c = 0.00002$ M) corresponds to the spectrum of α' -nitraminonicotine; at the higher concentration ($c = 0.0001$), the absorption curve is close to that of α -nitraminonicotine.

EXPERIMENTAL

α -Amino- β' -nitronicotine *. α -Aminonicotine ground to a powder (1.75 g) was slowly added, with stirring and cooling with water, to 7.5 ml of sulfuric acid (monohydrate). The solution was cooled to -10° and 0.47 ml of HNO_3 (sp. gr. 1.51) was added dropwise with stirring. The solution was kept for one hour at the same temperature and one hour at a temperature of from -10 to 20° ; then it was gradually heated during 2 hours on the water bath to $\sim 100^\circ$, at which temperature it was kept for one hour and it was then, after cooling, poured onto 25 g of ice. The addition of a 20% solution of NaOH yielded a precipitate which was rapidly filtered off and washed with water. A yield of 0.5 g (26%) of an impure nitro derivative was obtained. After recrystallization from absolute alcohol (with the addition of activated carbon), almost colorless crystals with m.p. $171 - 172^\circ$ were obtained. Found: C 53.97, 54.15; H 6.24, 6.30; N 25.48, 25.56%. $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2$. Calculated: C 54.04; H 6.35; N 25.21%.

The alkaline solution was neutralized with sulfuric acid and evaporated to dryness. A product was extracted with alcohol from the dry residue, the alcohol was distilled off, the residue dissolved in a small volume of water, and the solution was saturated with potash. A dark oily layer separated. The product was extracted with hot benzene; on removal of the solvent, crystals were obtained which, after recrystallization from *n*-octane had m.p. $121 - 122^\circ$. The product gave no depression in a mixed melting point with pure α -hydroxynicotine **. The yield of α -hydroxynicotine was $\sim 52\%$. The picrate of α -amino- β' -nitronicotine was prepared: m.p. $256 - 257^\circ$ (with decomposition, from alcohol). Found: C 42.38, 42.36; H 3.66, 3.71; N 21.62, 21.65%. $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$. Calculated: C 42.57; H 3.80; N 21.72%.

α' -Amino- β' -nitronicotine. The experiment was carried out under the conditions for the nitration of the α -amino isomer, starting from 7 g of α' -aminonicotine. A yield of 0.75 g (8.5%) of unpurified nitro derivative was obtained. After recrystallization from absolute alcohol, yellow crystals with m.p. $112 - 113^\circ$ were obtained. Found: C 54.38, 54.15; H 6.30, 6.37; N 25.42, 25.56%. $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2$. Calculated: C 54.04; H 6.35; N 25.21%. In addition, 4.2 g of a substance with m.p. $101 - 103^\circ$ (from *n*-octane) was isolated. This product gives no depression of the melting point in admixture with pure α' -hydroxynicotine ***. The yield of α' -hydroxynicotine was 60%. The picrate of α' -amino- β' -nitronicotine was prepared: m.p. $250 - 252^\circ$ (with decomposition, from alcohol and from acetone). Found: C 42.52, 42.79; H 3.69, 3.71; N 22.05, 22.05%. $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$. Calculated: C 42.57; H 3.8; N 21.72%.

α' -Nitraminonicotine. To a solution of 3.5 g of α' -aminonicotine in 7.5 g of sulfuric acid (monohydrate) at a temperature of -10° and with mixing, 0.9 ml of nitric acid (sp. gr. 1.52) was added dropwise, after which the solution was held for 30 min. at $-10 - 0^\circ$ and then poured on 60 g of ice. The acidic solution was treated with an excess

* α -Amino- β -nitronicotine was first obtained by Popov [19].

** According to data in the literature, the m.p. of α -hydroxynicotine is $121 - 123^\circ$ [7].

*** According to data in the literature, the m.p. of α' -hydroxynicotine is $103.5 - 104^\circ$ [7].

of BaCO_3 , the precipitate of BaSO_4 was filtered off and washed several times with hot water. The washing waters were combined with the main filtrate. The solution was neutralized, filtered and evaporated to dryness in vacuo. By repeated treatment with hot absolute alcohol, 3.76 g of almost colorless crystals were extracted from the dry residue; m.p. 193 - 194° (with decomposition, from absolute alcohol). Found: C 54.14, 54.12; H 6.22, 6.26; N 25.19, 25.10%. $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2$. Calculated: C 54.04; H 6.35; N 25.12%. Yield of α' -nitraminonicotine 85.6%. The picrate had m.p. 201 - 202° (with decomposition, from water). Found: C 42.58, 42.41; H 3.85, 3.81; N 21.52%. $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$. Calculated: C 42.57; H 3.80; N 21.72%.

α' -Nitraminonicotine was obtained from α -aminonicotine under the conditions of formation of the α' -isomer, with the sole difference that, instead of monohydrate, ~ 95% sulfuric acid was used and the relative amount of the acid was increased two-fold. A colorless nitramino derivative with m.p. 170° (with decomposition) was obtained; yield 86-87%. Recrystallization from absolute alcohol did not change the melting point. Found: C 53.93, 53.99; H 6.57, 6.48; N 25.40, 25.60%. $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2$. Calculated: C 54.04; H 6.35; N 25.21%. The picrate had m.p. 206.5-207.5° (with decomposition, from water). Found: C 42.73, 42.51; H 3.79, 3.74; N 21.30, 21.38%. $\text{C}_{10}\text{H}_{14}\text{N}_4\text{O}_2 \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$. Calculated: C 42.57; H 3.80; N 21.72%.

α - and α' -Nitraminonicotines possess acidic properties: on treating their concentrated aqueous solutions with a 50% solution of NaOH, crystalline salts separated, the composition of which was not determined.

Action of sulfuric acid on α' -nitraminonicotine. To 36 ml of ~ 95% sulfuric acid, with water cooling and periodic stirring, 9 g of α' -nitraminonicotine was slowly added. After 40 hours the solution was heated for 2 hours at 40°, then for 1.5 hours at a temperature gradually increasing to 100°, and, finally, for 20 minutes at 100°. A yield of 667 ml of gas* (73.3%) was obtained. The solution was poured onto 120 g of ice. On the addition of a 20% solution of NaOH, 1.75 g of α' -amino- β -nitronicotine separated; m.p. 112-113°; yield 19.4%. From the alkaline solution, 5.4 g of impure α' -hydroxynicotine was isolated by the method described above; yield 74.5%. On repeatedly passing measured volumes of the gas collected over red-hot reduced granular copper, it was established from the weight of oxygen that the gas contained ~ 89% of nitrous oxide.

Action of sulfuric acid on α -nitraminonicotine. α -Nitraminonicotine (1.3 g) was subjected to treatment with sulfuric acid under the conditions of the experiment with the α' -isomer, with the sole difference that the α -nitraminonicotine was added to the sulfuric acid at 0°. The yield of gas was 70.5 ml (53.8%). The gas contained ~ 94% of nitrous oxide. From the reaction solution were isolated 0.48 g (37%) of α -amino- β' -nitronicotine and 0.53 g (~51%) of α -hydroxynicotine.

Action of acetic anhydride on α' -nitraminonicotine. To a mixture of 2 g of α' -nitraminonicotine and 6.4 ml of glacial acetic acid on the boiling water bath, were added gradually 1.4 ml of acetic anhydride and 6.4 ml of glacial acetic acid, after which the mixture was boiled for 45 minutes in an oil bath. Considerable resinification was observed and 141.5 ml of gas was evolved (yield 70.2%). It was found by quantitative determination that the gas contained ~ 89% of nitrogen and ~ 11% of nitrous oxide. A 10% solution of NaOH was added to the reaction mixture with cooling until it possessed a weakly alkaline reaction; the solution was extracted with benzene, saturated with potash, and again extracted with benzene, and then with alcohol. No individual compounds could be isolated from the benzene solutions. The alcoholic solution, containing a large quantity of resinous products, was dried over calcined potash. After removing the alcohol, a product was extracted from the residue with boiling chloroform. The chloroform was distilled off and from the residue now obtained a product was extracted with boiling n-octane in order to free it from resin. After removal of the octane, a faintly colored viscous product was isolated, from an aqueous solution of which a picrate of m.p. ~ 150° was obtained by fractional precipitation. After recrystallization from water it had m.p. 212.5 - 215.5°. The picrate of a pure sample of α' -hydroxynicotine prepared for comparison had m.p. 214.5 - 215.5°. For the latter were found: C 47.18, 47.11; H 4.09, 4.08; N 17.10, 17.32%. $\text{C}_{10}\text{H}_{14}\text{N}_2\text{O} \cdot \text{C}_6\text{H}_3\text{N}_3\text{O}_7$. Calculated: C 47.18; H 4.21; N 17.19%. No depression of the melting point was observed for a mixture of these picrates.

Action of acetic anhydride on α -nitraminonicotine. α -Nitraminonicotine (1.3 g) was treated with acetic anhydride under the conditions of the experiment with the α' -isomer. A yield of 60.7 ml of gas (46.3%) was obtained. The gas contained 72.6% of nitrogen and 17.4% of nitrous oxide.

* Here and elsewhere the volume of gas is given for normal conditions.

Action of acetic anhydride on an equimolar mixture of triethylamine and α -nitraminopyridine. To a solution of 5 g of triethylamine in 5.7 ml of glacial acetic was added 6.9 g of α -nitraminopyridine, and 9.4 ml of acetic anhydride and 2.9 ml of glacial acetic acid were run in. The mixture was gradually heated in the course of one hour on the water bath to 100° and was maintained at 100° for ~ 30 min. The reaction was accompanied by the evolution of heat. A yield of 887 ml of gas (80%) was obtained. The gas contained 89.4% of nitrogen and 10.6% of nitrous oxide. The reaction mixture was acidified with 10% sulfuric acid. The acid solution (A) was repeatedly shaken out with ether. The ether was distilled off from the ethereal extract, and the residue was treated with boiling absolute alcohol. On removing the solvent, the residue was dissolved in a small amount of water to free it from acetic acid; the solution was saturated with potash, repeatedly washed with ether, and the ethereal solution was dried over calcined potash. After removal of the ether, the residue was distilled, yielding 1.18 g of a first fraction with b.p. 180-187° (760 mm), 0.8 g of a second fraction with b.p. 166-172° (15 mm), and 0.2 of resinous residue. The first fraction consisted of diethylacetamide; yield, 20.7% *. Found: N 12.17%. $C_6H_{13}NO$. Calculated: N 12.16%. In order to confirm its structure, part of the first fraction was saponified with 25% hydrochloric acid (100°, 6 hours). The melting point of the hydrochloride obtained was 221-222° (from absolute alcohol). The product gave no depression of the melting point in admixture with diethylamine hydrochloride.

On standing, the main part of the second fraction crystallized. The crystals were pressed out; m.p. 104-106° (from benzene). The product gave no depression of the melting point in admixture with a pure sample of α -hydroxypyridine.

The acidified reaction solution (A), after its extraction with ether, was treated with K_2CO_3 to saturation and again washed with ether. The ethereal solution was dried over calcined potash and distilled with a fractionating column. A fraction with b.p. 82-86° was collected with a yield of 1 g *. The picrate of this product melted at 171-173° and gave no depression of the melting point in admixture with triethylamine picrate.

We established in a blank experiment that triethylamine undergoes practically no change on heating with acetic anhydride in glacial acetic acid (2 hours at 100°). Similarly, it undergoes no change on the action of nitrous acid in the presence of acetic anhydride and acetic acid under the temperature conditions of the experiment described here. Hence it follows that the formation of diethylacetamide in this reaction, apparently, is connected with the presence of the nitramino group.

Action of acetic anhydride on a mixture of N-methylpiperidine and α -nitraminopyridine. The experiment was carried out under the conditions of the experiment with triethylamine described above. The yield of gas was 82.4% and its composition was: 90.3% of N_2 and 9.7% of N_2O .

SUMMARY

1. On nitration of α - and α' -aminonicotines with HNO_3 in concentrated H_2SO_4 , the corresponding nitramino derivatives are formed as the primary reaction products.
2. α - and α' -Nitraminonicotines decompose on heating in concentrated H_2SO_4 to form N_2O and α - and α' -hydroxynicotines, and, to a smaller extent, isomerize into α - and α' -amino- β -nitronicotines; on heating with acetic anhydride in glacial acetic acid they decompose to form not N_2O but, mainly, nitrogen.
3. An equimolar mixture of α -nitraminopyridine and a tertiary aliphatic amine (triethylamine or N-methylpiperidine) on being treated similarly yields not N_2O but, mainly, nitrogen.

* In other experiments carried out similarly, the yield of diethylacetamide varied from 12.3 to 25%.

** Unreacted triethylamine, in view of its high volatility, could be only partially recovered. In order to recover it more completely, in an experiment carried out in a similar manner, the reaction solution, acidified with hydrochloric acid, was washed with ether and evaporated to dryness. The dry residue was treated with an excess of a 50% solution of NaOH and the triethylamine was distilled into hydrochloric acid. On evaporating the hydrochloric acid solution, all the unreacted triethylamine was recovered in the form of the hydrochloride.

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CATALYTIC POLYMERIZATION OF OLEFINS

13. POLYMERIZATION OF ISOBUTYLENE IN THE PRESENCE OF SOME SILICAGEL SAMPLES

Ya. T. Éidus and B. K. Nefedov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences, USSR

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The polymerization of isobutylene in the presence of natural [1, 2] and synthetic aluminum silicates [3] has been studied in detail by several authors. The polymerization proceeds readily at atmospheric pressure over a broad temperature range with the formation of products analogous in composition to the products of isobutylene polymerization under acidic conditions. We showed earlier that isobutylene is polymerized in the presence of red clay [4] and kieselguhr (from Kistatibi) [5], which approximates synthetic aluminum silicate cracking catalyst in its activity.

Silica, an essential component of aluminum silicates, proves to be inactive (in the form of thermally activated silicagel) in the polymerization reaction of isobutylene at room temperature under atmospheric pressure [2]. However, it was later found that silicagel shows some polymerizing action on olefins, e.g., on pentene at 200-380° [6] and on highly-branched olefins e.g., on diisobutylene even at room temperature [7]. The catalytic activity of silicagel in the polymerization, isomerization, and other reactions of olefins often is explained by the presence of aluminum oxide, i.e., the aluminum silicate described [8, 9], in the mixture.

Investigation of the catalytic activity of samples of different types of silicagel in the polymerization of isobutylene at elevated temperature was the primary goal of our work

EXPERIMENTAL

The apparatus and methods of conducting the experiments did not differ from those described before [4, 10]. The experiments on the polymerization of isobutylene were conducted in a circulating system at atmospheric pressure with a volume velocity of isobutylene feed about 100 hr^{-1} in a glass reaction tube with 15 mm internal diameter. The catalyst volume in the tube was 30 ml.

Influence of the type of silicagel and of reaction temperature on the yield of products of isobutylene polymerization. Samples of some types of silicagel from the Voskresensk chemical plant were used as catalysts [11], namely coarsely porous: KSK (particle size 4-5 mm), ASK, MSK, and ShSK (80-100 mesh) and finely porous: ASM, KSM (sample 1) and ShSM (sample 1) (80-100 mesh), KSM (3-4 mm, sample 2) and ShSM (2-3 mm, sample 2). The catalysts did not undergo any preliminary treatment before the experiments. A series of experiments in polymerizing isobutylene at 190° was conducted with each of these samples and the yield of liquid polymer (freed of C_4 hydrocarbons) was determined. Some samples of catalyst were treated in an air stream at 300° for 3-5 hr after several polymerization experiments in order to regenerate catalyst activity and then used again in the same reaction. The duration of each experiment was 7 hr.

The results obtained, given in Table 1, show different catalytic activity for the coarse and fine samples of silicagel. Coarse silicagel samples ASK, MSK, and ShSK showed little activity under the conditions used, notwithstanding their small particle size. The yield of liquid polymer in the first experiments (first 7 hr) was 0.9-1.3% of the feed isobutylene (expts. 1.5 and 7) and in further experiments (the following 7 hr) fell to 0.4-0.8% (expts. 2, 6, and 8). Silicagel ASK treated with air at 300° (and also at 500°) was not reduced in activity, but displayed increased adsorptive power, which is seen by the increase of gas uptake from 1.0% in expt. 2 to 11.1% in expt. 3. Only sample KSK, in spite of its significantly large particle size, of the coarse silicagels was active in the polymerization of isobutylene. The yield of liquid polymer from fresh and regenerated surfaces of this sample were nearly equivalent and were 9.3-10.6% from feed isobutylene (expts. 9, 12, and 15). In the first hour of the experiment the catalyst adsorbed

TABLE 1. Influence of the Type of Silicagel on the Yield of Products from Isobutylene Polymerization

Expt. No.	Sili-cagel	Gas up-take, %	Yield of liquid polymer, % from feed		Expt. No.	Sili-cagel	Gas up-take, %	Yield of liquid polymer, % from feed	
			iso-butylene feed	iso-butylene reacting				iso-butylene feed	iso-butylene reacting
Coarse silicagel					Fine silicagel				
1	ASK	1,8	1,3	—	18	ASM	35,8	25,2	70,2
2	»	1,0	0,4	—	19	»	22,2	20,4	90,5
3*	»	11,1	0,8	—	20	»	15,2	15,2	76,5
4*	»	5,8	0,8	—	21*	»	20,2	17,3	87,0
5	MSK	18,2	1,0	—	22	»	13,4	12,2	91,5
6	»	3,7	0,8	—	23	KSM(1)	54,5	44,0	85,0
7	ShSK	1,1	0,9	—	24	»	43,2	36,6	100
8	»	4,5	0,4	—	25	KSM(2)	39,0	31,4	80,5
9	KSK	18,3	10,6	59,0	26	»	19,1	17,6	90,5
10	»	17,4	8,1	45,5	27*	»	8,0	3,0	38,4
11	»	20,0	3,8	19,3	28	ShSM(1)	60,8	54,4	91,0
12*	»	15,4	9,3	60,5	29	»	43,5	41,0	94,0
13	»	12,7	5,2	41,0	30	»	33,5	31,0	93,0
14	»	5,8	5,0	89,5	31	ShSM(2)	57,0	42,5	74,0
15*	»	24,0	9,9	41,0	32	»	32,2	31,6	97,5
16	»	10,0	6,7	67,0					
17	»	3,6	3,6	100					

* Catalyst was treated with air at 300° before the experiment.

TABLE 2. Influence of Reaction Temperature on the Yield of Isobutylene Polymerizate in the Presence of Silicagel KSM

Expt. No.	Reaction temp. °C	Gas up-take, %	Yield of liquid polymer, % from iso-butylene		Expt. No.	Reaction temp. °C	Gas up-take, %	Yield of liquid polymer, % from iso-butylene	
			feed	reacted				feed	reacted
18	100	65,4	39,4	60,5	30	300	27,4	18,6	68,0
19	100	39,2	39,2	100,0	31**	300	42,6	39,2	92,2
20	100	43,0	36,6	85,0	32	300	35,1	10,9	31,1
21	100	38,3	32,9	85,3	33	400	67,2	16,3	24,2
22	200	55,6	45,0	80,6	34	400	51,3	16,6	32,5
23	200	39,8	38,4	96,3	35	400	—	9,6	—
24	200	34,6	29,7	85,0	36	400	7,8	7,8	100
25	200	29,2	25,8	88,6	37**	400	19,2	23,3	—
26*	200	32,0	25,7	80,5	38	400	13,8	16,7	—
27	200	18,9	10,0	53,0	39	500	7,4	22,6	—
28	300	46,8	35,4	75,6	40	500	14,0	8,8	—
29	300	33,7	28,0	83,0					

* Catalyst was treated with air at 300° before the experiment.

** Catalyst was treated with air at 400° before the experiment.

isobutylene strongly; this is evident from the high value of gas uptake in comparison with the yield of reaction products from feed and from the comparatively small yield from reacted isobutylene (expts 9-13, 15, and 16). The catalyst activity rapidly fell, along with absorptive capacity, as a measure of the reaction course. Gas uptake and yield from feed isobutylene have similar values, but the yield from reacted isobutylene rises to 90-100% (expts. 14 and 17). An important characteristic of silicagel KSK is that it is easily and completely regenerated by treatment with air at 300°.

All of the samples of silicagel used were active in polymerizing isobutylene. In comparison to samples of the same particle size [ASM, KSM (1), and ShSM (1)] it is evident that sample ShSM is most active and ASM is least. The yield of liquid reaction products in the first hour of the experiment was: ASM, 25.2%; KSM, 44.0%, and ShSM,

54.4% (expts. 18, 23, and 28). The reaction occurs selectively with yields of 70-100% of reacting isobutylene. Samples KSM and ShSM (2) with larger particle sizes were somewhat less active. But it is necessary to point out that, unlike KSK, fine silicagels are not regenerated by air at 300° (expts. 21 and 27).

Investigation of the effect of reaction temperature on the yield of polymerization products was carried out in the interval from 100 to 500° with silicagel KSM (1). A separate portion was used for contact at each temperature.

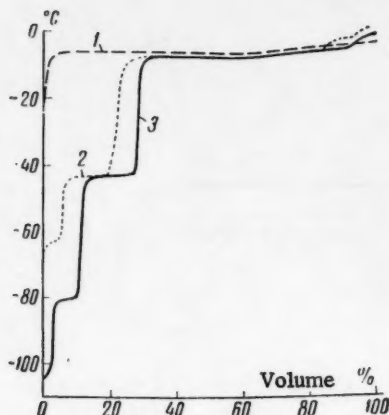


Fig. 1. Curve for low-temperature fractionation of feed isobutylene (line 1) and exit gases in isobutylene polymerization in the presence of silicagel KSM at temperatures of 400° (curve 2) and 500° (curve 3).

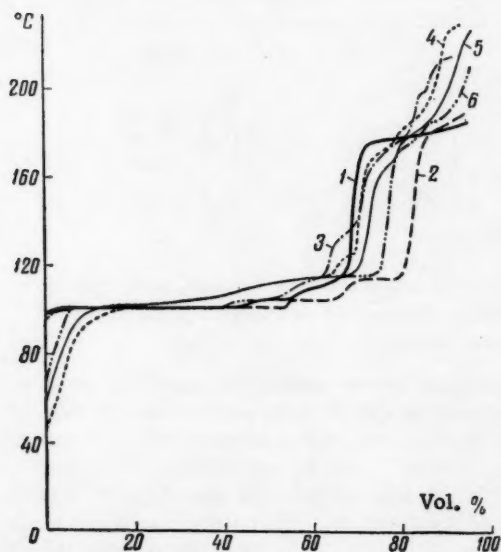


Fig. 2. Distillation curve for polymer obtained in the presence of silicagel: 1) KSK; 2) ASM; 3) KSM; 4) KSM (2); 5) ShSM (1); 6) ShSM (2).

tetramers and higher polymers. In the fraction boiling 101-106°, the ratio of 2, 4, 4-trimethylpentene-1 (b.p. 101-102°) to 2, 4, 4-trimethylpentene-2 (b.p. 104-106°) is about 4 : 1. The content of other octene isomers (fraction be-

TABLE 3. Composition of Exit Gases from Isobutylene Polymerization over Silicagel KSM

Composition of exit gas, vol. %	Reaction temperature, °C		
	300	400	500
CO ₂	0,0	0,0	0,2
C _n H _{2n}	77,4	71,4	76,0
O ₂	0,2	0,4	0,2
CO	2,4	1,4	1,6
H ₂	2,4	5,4	8,0
C _n H _{2n+2}	17,0	20,0	12,8
N ₂	0,6	1,4	1,2

From table 2, in which the results of the experiments are presented, it is evident that polymerization goes readily even at 100° with an initial polymer yield of approximately 40% based on feed isobutylene. The maximum yield (45%) is obtained at 200°. At more elevated reaction temperatures the catalytic stability of the substrate, which was regenerated by treatment with air at 400°, for a short time, decreased. As is shown by analysis of exit gases (Table 3) and by low-temperature fractionation (Fig. 1), isobutylene polymerization at 500° is accompanied by decomposition which gives rise to the formation of hydrogen and C₂-C₃ saturated and unsaturated hydrocarbons. The small [apparent] uptake of gas during the reaction is thus explained.

Effect of the type of silicagel and of reaction temperature on the composition of polymerization products. In longer experiments with each of the active silicagel samples at 190° (but with KSK (1) in the interval from 100 to 400°) 50-100 ml of liquid polymer was prepared, which [after drying over calcium chloride and elimination of gases (C₄H₈) by fractionation] was separated through a column filled with triangular copper coils (of 40 theoretical plates efficiency). The narrow fraction boiling below 130° was separated, and the high-boiling residue was distilled from a Wurtz flask. In Table 4 are presented the properties of polymer obtained from different silicagel samples at 190°; in Table 5 are the yields of the various narrow fractions on distillation; on Fig. 5 are the distillation curves for these polymers. From these data it is apparent that the liquid polymer obtained from sample KSK is 57 volume-% of dimers and approx. 25% of isobutylene trimers and that it contains no products boiling below 101°, i.e., C₅-C₇ hydrocarbons, or above 188°, i.e.,

TABLE 4. Properties of Isobutylene Polymers Obtained in the Presence of Different Silicagel Samples

Polymerizate property	Silicagel					
	KSM	ASM	KSM(1)	KSM(2)	ShSM(1)	ShSM(2)
d_4^{20}	0,7143	0,7001	0,7145	0,7091	0,7061	0,7071
n_D^{20}	1,4164	1,4160	1,4200	1,4201	1,4190	1,4221
Initial boiling, °C	101	94,5	46	56	68	59
Final boiling, °C	188	190	227	215	207	228

TABLE 5. Contents of Fractions According to Catalysts (Vol. %)*

Limits of boiling range, °C	Silicagel					
	KSK	ASM	KSM(1)	KSM(2)	ShSM(1)	ShSM(2)
< 101	0,0	8,3	18,0	16,8	7,6	13,2
101-102(2,4,4-trimethylpentene-1)	46,2	44,0	9,8	12,0	26,4	12,4
104-106(2,4,4-trimethylpentene-2)	10,9	8,6	4,9	9,9	10,1	8,6
106-130(isomeric octenes)	11,9	14,3	34,3	29,5	26,8	30,8
> 130(trimers and polymers)	24,4	14,3	22,4	25,6	17,3	24,4

* Intermediate fractions are not presented in the table.

TABLE 6. Properties of Isobutylene Polymer Obtained over Silicagel KSM at Different Temperatures

Polymer property	100°	300°	400°
n_D^{20}	1,4270	1,4262	1,4431
Initial boiling, °C	75,5	34,2	35,5
Final boiling, °C	> 200	> 280	> 280
Bromine number	—	167,5	1320

TABLE 7. Content of Fractions in Polymer (Vol. %) Obtained over Silicagel KSM at Different Temperatures

Limits of boiling range, °C	100°	300°	400°
< 101	2,8	18,4	24,4
101-106	15,1	16,7	9,0
106-130	5,9	40,4	32,6
> 130 (trimers and polymers)	69,5	21,3	30,3

tween 106 and 130°) is about 12%. The liquid polymer obtained from the less active fine silicagel, sample ASM, is similar in composition to the polymer obtained over sample KSK. The difference is only that the yield of trimers falls to 14.3% and the fraction originating from 94.5 to 101° comprises 8.3%.

Reaction products obtained on more active samples of fine silicagels contain considerably less of the fraction containing 2, 4, 4-trimethylpentene-1, which falls to 9.8% in the case of sample KSM (1), and considerably more of the trimer octenes* (27-34%). Also, the fraction containing C_5-C_7 hydrocarbons rises in isolated cases (sample KSM 1) to 18%. The initial boiling point of these polymers falls sharply (46-48°, Table 4), but the final boiling point rises (207-228°). The separate narrow-boiling fractions, given in Table 5, from different polymers differ little in their constants. The fraction with boiling point 101-102° has d_4^{20} 0.7133-0.7144 and n_D^{20} 1.4089-1.4105 and corresponds to 2, 4, 4-trimethylpentene-1 (literature data [12]; b.p. 101.36°; d_4^{20} 0.7150; n_D^{20} 1.4086); the fraction 104-106° d_4^{20} 0.7198-0.7244; n_D^{20} 1.4128-1.4185 and corresponds to 2, 4, 4-trimethylpentene-2 (literature data [12]; b.p. 104.85°; d_4^{20} 0.7212; n_D^{20} 1.4160). The constants of other broader fractions vary within the following limits: fraction boiling below 101°: d_4^{20} 0.6888-0.7094; n_D^{20} 1.4040-1.4082 (hydrocarbons boiling below C_8); fraction from 106 to 130°: d_4^{20} 0.7313-0.7460; n_D^{20} 1.4200-1.4235; fraction above 130°: d_4^{20} 0.7614-0.7881; n_D^{20} 1.4336-1.4470.

As supplements to the isobutylene polymerization experiments over silicagel KSM (1) at 190° (Tables 4 and 5),

*Probably should be "dimeric octenes." (Publishers note).

protracted experiments with this same silicagel were conducted in the temperature interval from 100 to 400°. The properties of the polymers obtained are given in Table 6, the yields of different fractions on distillation are in Table 7, and the distillation curves for the polymers are on Fig. 3. From the data presented it is seen that with increasing reaction temperature the fraction of hydrocarbons boiling below dimers ($< 101^\circ$) is increased with lowering of their initial boiling point. The total fraction of low-boiling dimers (b.p. $101-106^\circ$, n_D^{20} 1.4092-1.4140; d_4^{20} 0.7144-0.7209) decreases sharply (to 9.0%) at 400°, but the fraction of higher-boiling isomeric dimers (b.p. $106-130^\circ$, n_D^{20} 1.4142-1.4232; d_4^{20} 0.7228-0.7424) was at a maximum (40%) in the polymer obtained at 300°. The trimer fraction was maximal at 100° reaction temperature; this fraction (b.p. $177-200^\circ$, n_D^{20} 1.4332; d_4^{20} 0.7611) was 62.6% of the polymer. A solid residue, 3-4%, remained from fractionation of the polymer obtained at 300° and 400°. The polymer formed at 400° contained a fraction boiling $142-178^\circ$; n_D^{20} 1.4855; d_4^{20} 0.8466, including aromatic hydrocarbons (positive formolite reaction).

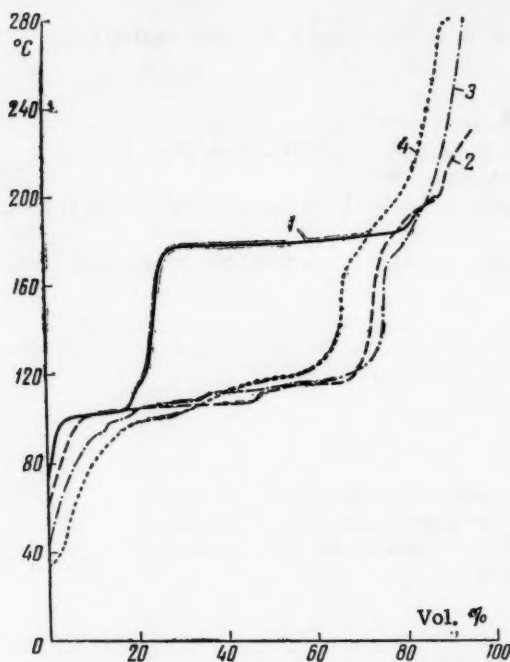


Fig. 3. Boiling curve for polymers obtained in the presence of silicagel KSM at 100° (curve 1); 200° (curve 2); 300° (curve 3); 400° (curve 4).

that the specific surface is not the deciding factor, as shown by the many times' greater activity of silicagel ShSM than KSK, the specific surfaces of which are 98 and 194 m^2/g [9]. Silicagel ShSK with a specific surface of 192 m^2/g is also inactive. We showed earlier [13] that of all the silicagel types we studied only KSK was useful as a carrier for NiO catalysts, which are active in ethylene polymerizations and that this activity is associated to a known extent with the admixed aluminum oxide.

SUMMARY

- Investigation of the catalytic activity of different types of silicagels in polymerization of isobutylene at 190° and atmospheric pressure showed that fine types (ASM, KSM and particularly ShSM) and, to a lesser extent, only one coarse silicagel (KSK) are active.
- Polymerization products obtained in the presence of samples KSK and ASM are mainly 2, 4, 4-trimethylpentene-1 (to 45%), 2, 4, 4-trimethylpentene-2 (10%) and trimers (15-25%). Polymerization on the remaining types of silicagels studied was accompanied by skeletal isomerization and formation of non-integral polymers (C_5-C_7 hydrocarbons).

The results obtained show that all of the fine silicagels, but only KSK (to a lesser extent) among the coarse silicagels, are active in the polymerization of isobutylene at 190° under atmospheric pressure. On this silicagel, and also on the less active of the fine silicagels (sample ASM), the actual isobutylene polymerization proceeds, and dimers (primarily 2, 4, 4-trimethylpentene-1) and trimers predominate in the polymer composition.

On fine samples KSM and ShSM considerable amounts of higher-boiling isomeric octenes are also formed, but these polymers (C_5-C_7 hydrocarbons) are not multiples of the feed olefin. The silicagel samples used exhibit little catalytic strength; thus only one silicagel (KSK) is regenerated by treatment with air at 300°. A study of the effect of temperature on the course of isobutylene polymerization in the presence of silicagel KSM in the interval from 100 to 500° showed that the maximum yield of polymer is reached at 190°, which is fairly close to the optimum temperature found earlier for Kisatibi kieselguhr [5], i.e., natural aluminum silicate. This similarity, apparently, is clarified by the fact that the activity of the silicagels studied in the polymerization of isobutylene is due to the admixture of Al_2O_3 , i.e., the availability of aluminum silicate. Thus, in silicagels KSK, ShSK, and ShSM are contained, respectively, 0.79, 1.05, and 1.42% Al_2O_3 (based on absolutely dry substance) [9]. The structure of the silicagel surface also plays a large role, since a number of silicagels containing Al_2O_3 are inactive. It is necessary to point out

3. The optimum reaction temperature (in the interval from 100 to 500°) was 190°.
4. Only sample KSK, among the silicagels studied, is regenerated by treatment with air at 300°.

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All abbreviations of periodicals in the above bibliography are letter-by-letter transliterations of the abbreviations as given in the original Russian journal. Some or all of this periodical literature may well be available in English translation. A complete list of the cover-to-cover English translations appears at the back of this issue.

THE SYNTHESIS OF VINYLPIRROLIDONE

S. N. Ushakov, V. V. Davidenkova and V. V. Lushchik

Institute of Large Molecular Compounds, Academy of Sciences, USSR

Translated from *Izvestiya Akademii Nauk SSSR, Otd. Khimicheskikh*

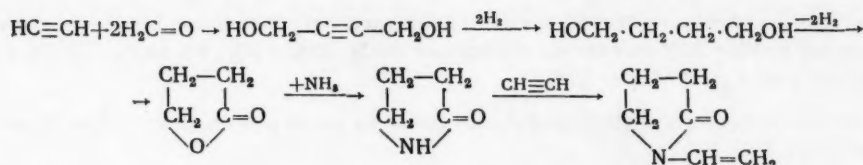
Nauk, 1961, No. 5,

pp. 901-905, May, 1961

Original article submitted April 9, 1960

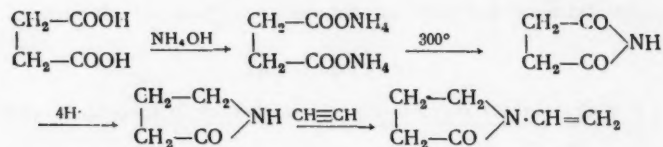
At the present time vinylpyrrolidone is widely used for the production of polymers and various co-polymers which are used as plasma substitutes, as agents for prolonging the action of drugs, as detoxicators, in the production of beer and wine, in the cosmetic and textile industries, for the preparation of adhesives, as dispersing agents, etc.

The synthesis of vinylpyrrolidone was first achieved by Reppe [1] according to the following scheme. It consisted of five steps:



The commercial synthesis is rather complicated [2]. Butynediol is prepared in a column in which 30 - 35% formalin and acetylene are introduced in the presence of acetylenides of bismuth or copper at 90 - 100°. The crude (35%) butynediol solution obtained is distilled and hydrogenated over a copper-nickel catalyst at a temperature of 70 - 140° and a pressure of 200 - 300 atm. Then the resulting butanediol is dehydrogenated to γ -butyrolactone at 200° in the presence of copper (on silica); this product is distilled and treated with anhydrous ammonia in an autoclave at 230° and a pressure of 40 atm (in the batch method) or at 80 - 90 atm (in the continuous process). After vacuum distillation the pyrrolidone is vinylated, in the presence of anhydrous caustic potash as a catalyst, at 140 - 160° and 20 - 25 atm in an atmosphere of nitrogen. Shostakovskii and others [3] prepared vinylpyrrolidone in an analogous manner. α -Pyrrolidone is obtained by the reaction of butyrolactone (3 M) with liquid ammonia (5 M) at 200 - 220° and 40 - 50 atm during a period of 15 hours. Yur'ev [4] studied the catalytic conversion of butyrolactone to α -pyrrolidone by reaction with ammonia at 350° in the presence of Al_2O_3 .

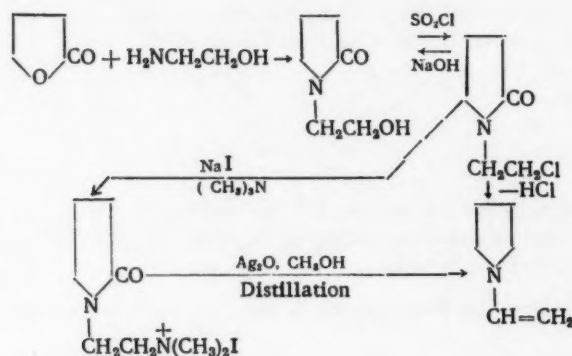
In 1952 the authors synthesized N-vinylpyrrolidone, starting with succinic acid as follows:



Succinimide was obtained by heating the ammonium salt of succinic acid at 300°. The product was distilled (275 - 289°) and recrystallized from 95% ethyl alcohol. The succinimide was reduced electrolytically to pyrrolidone in a 50% aqueous solution of sulfuric acid at lead electrodes with a current density of 80 - 90 mA/cm² and a current concentration of 900-100 A/liter. Vinylation of the pyrrolidone was carried out in an autoclave in a solution of dioxane and in the presence of potassium pyrrolidone at 15-25 atm and 125 - 132°. The method described, which was carried out in a cell arrangement, is more convenient than Reppe's method. The vinylpyrrolidone which was systematically produced, was used for the synthesis of polymers which gave satisfactory results when solutions of them were used as blood substitutes in the Leningrad Institute for Blood Transfusion [5]. Independently of the authors' work and almost

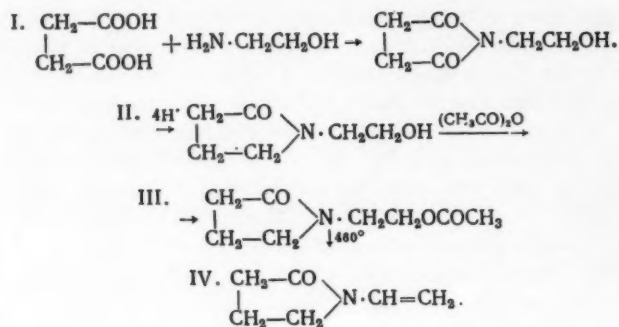
simultaneously, information was published on the preparation of pyrrolidone from succinic acid and ammonia by means of succinimide [6]. However in this synthesis, the final operation — the vinylation of pyrrolidone — is accomplished by the use of acetylene under pressure, which results in a number of difficulties.

In a number of cases it is expedient to use a synthesis of vinylpyrrolidone without the use of acetylene and high pressure. Vinylpyrrolidone may be prepared, for example, as follows [7]:



According to an American patent [9] when N-(β -hydroxyethyl) pyrrolidone is passed in the vapor state at reduced pressure and at 300 - 340° over activated aluminum oxide (93% Al_2O_3 , 2% Fe_2O_3 and 5% KOH), vinylpyrrolidone is obtained with a yield of up to 82%.

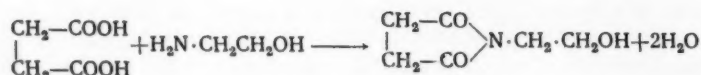
We achieved the synthesis of vinylpyrrolidone, without the use of pressure or acetylene, by starting with succinic acid, as follows:



Thus, starting with succinic acid and using readily available reactants (monoethanolamine and acetic anhydride, it is possible to prepare vinylpyrrolidone in four steps without using acetylene or high pressure.

EXPERIMENTAL

The synthesis of N-(β -hydroxyethyl) succinimide was carried out in accordance with the method described in [8] as follows:

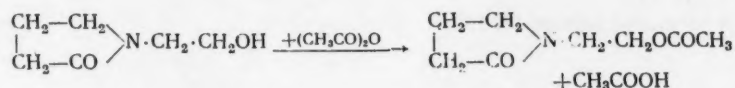


A mixture of equivalent quantities of succinic acid and monoethanolamine was heated for one hour at 150°. At the end of this period the temperature of the mixture had risen to 180° because of the heat of reaction, after which the process stopped. The reaction product was vacuum distilled and the fraction boiling at 176° (4 mm) was separated.

It solidified on cooling to a colorless crystalline substance. Yield 92% of theoretical [9].

The reduction of N-(β -hydroxyethyl) succinimide to N-(β -hydroxyethyl)-pyrrolidone was done electrically. The reduction process was carried out in a 50% solution of sulfuric acid at lead electrodes. The temperature of the solution during reduction was held within 1-5°, at a current density of 90 mA/cm² and a current concentration of 87 A/liter. The length of the reduction process was seven hours. After precipitation of the sulfuric acid from the reaction mixture (as CaSO₄) and distilling off the water, the remaining liquid product was distilled at reduced pressure. The fraction that boiled constantly at 166° (7 mm) was separated; its composition was: C 56.3; H 8.61; N 11.6; OH 11% (the nitrogen was determined by the Dumas semi-micro method; the OH groups by the acetylation method). The calculated values for N-(β -hydroxyethyl)-2-pyrrolidone are: C 56.7; H 8.68; N 11.0; OH 13%. Determination of the molecular weight by the cryoscopic method gave 121 (theoret. 127). The yield was 57% of theoretical.

Acetylation of N-(β -hydroxyethyl)-2-pyrrolidone was carried out as follows:



This was done by heating a mixture of it with a double excess of acetic anhydride to boiling for a period of five hours, after which the reaction product was distilled in vacuo. The fraction boiling at 135° (3 mm), was a colorless viscous liquid corresponding in composition to N-(β -acetoxyethyl)-2-pyrrolidone. The yield was 90% of theoretical. Found: C 55.89; H 7.78; N 8.39%. C₈H₁₃O₃. Calculated: C 56.12; H 7.63; N 8.17%.

The preparation of vinylpyrrolidone from N-(β -acetoxyethyl)-2-pyrrolidone by means of pyrolysis was carried out in a Pyrex reaction tube at 460° without the use of a catalyst. N-(β -acetoxyethyl)-2-pyrrolidone was introduced into the reaction tube (d = 28 mm, l = 500 mm) at a velocity of 20 drops per minute. The condensate was distilled in vacuo, which yielded a fraction boiling within the limits 83.5 - 84.5° (9 mm) (corresponding to vinylpyrrolidone), and a fraction boiling within the limits 151 - 154°. Analysis of the first fraction showed: N 13.02; C 64.74; H 8.2%. The corresponding calculated values for vinylpyrrolidone are: N 12.6; C 64.8; H 8.1%; n_D²⁰ 1.5132 and m.p. 12°. The product polymerizes under conditions analogous to those for pure vinylpyrrolidone. The yield of vinylpyrrolidone was 52% of theoretical. The second fraction consisted of original unchanged N-(β -acetoxyethyl)-2-pyrrolidone.*

SUMMARY

The synthesis of vinylpyrrolidone from succinic acid was accomplished without the use of acetylene or increased pressure.

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* In all stages of the process, waste products were not isolated.

STUDIES OF DERIVATIVES OF DIACETYLENE

REPORT No.8. THE REACTIONS OF ETHYNYLVINYL AND THIOETHYNYLVINYL ETHERS
WITH CARBONYL COMPOUNDS *

M. F. Shostakovskii, A. V. Bogdanova and G. I. Plotnikova

Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

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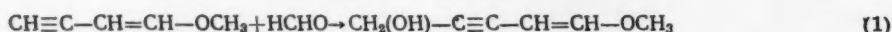
Nauk, 1961, No. 5,

pp. 905-909, May, 1961

Original article submitted January 19, 1960

Among the reactions of ethynylvinyl ethers and thioethynyl ethers that do not affect the triple bond may be included their reaction with carbonyl compounds [1]. Although the reactions of ethynylvinyl ethers with carbonyl compounds have only been described in the literature in the single case of ethylvinylmethyl ether, no description of analogous reactions with thioethynylvinyl ethers has yet appeared.

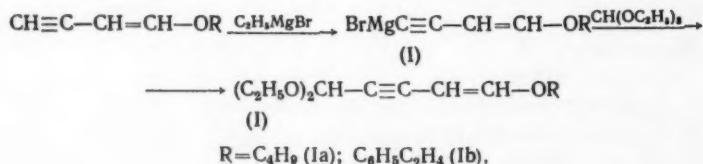
Weygand and Leube [2] studied the reaction of ethynylvinylmethyl ether with formaldehyde at various temperatures, and used the 1-methoxypentene-1-yne-3-ol-5 (equation 1) for the synthesis of 2-desoxy-d, 1-ribose and 2-desoxy-d, 1-xylose.



However, reactions of ethynylvinyl ethers with carbonyl compounds proceed most readily by means of the organo-magnesium complex. Thus, from ethynylvinylmethyl ether and the ethyl ester of orthoformic acid, Dornow [3] obtained the diethylacetal of 1-methoxypentene-1-yne-3-ol-5, which was the first etheracetal containing a pentene-1-yne-3 chain of carbon atoms that had been described in the literature. The author hydrated the etheracetal in a methyl alcohol solution, which lead to the formation of bisacetal containing a keto group; the latter cyclized to pyrone-4. In a similar manner the author [4] synthesized the ester of methoxybutenylcarboxylic acid.

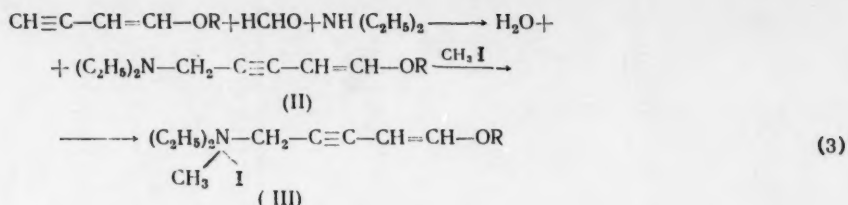
The simultaneous combination of formaldehyde and secondary amines with ethynylvinylmethyl ether was used for the preparation of ethynylvinyl aminoethers or Mannich bases [5, 6]. Thus the reaction of ethynylvinyl ethers with carbonyl compounds is of considerable interest, since it makes it possible to build up the chain of carbon atoms and increase the number of reaction centers in the molecule of the original ethers, thus increasing the synthetic possibilities of diacetylene derivatives.

In the present paper, along with a description of new examples of the reaction of ethynylvinyl ethers with the ethyl ester of orthoformic acid by means of the organo-magnesium complex (equation 2)

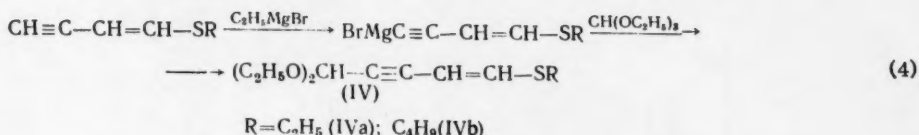


* For Report No. 7, see *Izv. AN SSSR, Otd. Khim. h.* (1960), 1514.

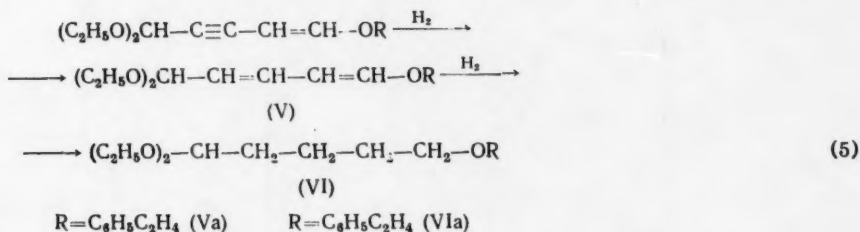
and also with formaldehyde and diethylamine (equation 3)



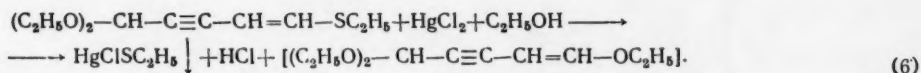
a description of the reaction of thioethynylvinyl ethers with the ethyl ester of orthoformic acid is also given. This reaction leads to the formation of a series of thioether acetals containing a pentene-1-yne-3 chain of carbon atoms (equation 4)



The formation of pentene-1-yne-3 etheracetals and thioetheracetals in good yield, which are stable on storage but undergo some conversion of the ethynylvinyl and thioethynylvinyl ethers, gives evidence that they still contain ethynylvinyl groups. Thus, 1, 1-diethoxy-5-phenylethoxypentene-4-yne-2, like ethylvinyl ether [7], partially and completely hydrogenates to the corresponding trialkoxypentadiene and trialkoxypentane derivatives (equation 5)



1, 1-Diethoxy-5-thioethylpentene-4-yne-2 reacts with an alcohol solution (equation 6) similarly to ethynylvinyl thioethers [8].



EXPERIMENTAL

Preparation of ethynylvinylphenylethyl ether. 17 g (47 % of theoretical) of ethynylvinylphenylethyl ether with b.p. 114 - 114.5° (4 mm); n_D^{20} 1.5522; d_4^{20} 1.0058; MR 54.73 were obtained from 10.7 g (0.21 M) of diacetylene, 52.2 g (0.42 M) of phenylethyl alcohol and 1.0 g of KOH at a bath temperature of 115 - 117° according to the method described previously [7]. The calculated value for $\text{C}_{12}\text{H}_{12}\text{O}$ is 41.6, MR 53.13. Analysis showed: C 83.47, 83.79; H 7.20, 7.22%. $\text{C}_{12}\text{H}_{12}\text{O}$, calculated: C 83.69; H 7.02%.

The reaction of ethynylvinyl ethers and thioethers with the ethyl ester of orthoformic acid. Into a three-necked flask, equipped with a stirrer, thermometer and dropping funnel, and containing an organo-magnesium compound obtained from 2.5 g Mg and 10.8 g $\text{C}_2\text{H}_5\text{Br}$ in absolute ether, cooled to $-8 \div -10^\circ$, 6.2 g (0.04 M) of ethynylvinyl-butyl ether was added drop by drop. After attaining room temperature, 14.0 g (0.09 M) of the ethyl ester of orthoformic acid were added to the mixture at such a rate that the temperature did not rise above 23 - 25°. Then the mix-

TABLE 1

Formula	Yield, %	(B.p. °C; pressure in mm)	n_D^{20}	d_4^{20}	MR		Found, %			Calculated, %		
					found	calculated	C	H	S	C	H	S
$C_4H_8O-CH=CH-C\equiv C-CH(OC_2H_5)_2$ (Ia)	70	133(3)	1,4698	0,9422	66,99	64,63	69,00	9,64		68,99	9,78	
$C_6H_5C_2H_5OCH=CH-C\equiv C-CH(OC_2H_5)_2$ (Ib)	45,3	112(7·10 ⁻³)	1,5223	1,0202	82,06	79,50	74,05	8,19	—	74,42	8,08	—
$C_2H_5S-CH=CH-C\equiv C-CH(OC_2H_5)_2$ (IVa)	58,8	127(4)	1,5125	0,9908	64,96	61,72	61,67	8,77	14,85	61,64	8,46	14,96
$C_4H_8S-CH=CH-C\equiv C-CH(OC_2H_5)_2$ (IVb)	80,0	147(4)	1,5045	0,9713	73,95	70,95	64,03	9,24	13,23	64,42	9,15	13,23

TABLE 2

Compound	(B.p. °C; pressure in mm)	n_D^{20}	d_4^{20}	MR		Found, %			Calculated, %		
				found	calculated	C	H	N	C	H	I
$C_{10}H_{17}O-CH=CH-C\equiv C-CH_2-N(C_2H_5)_2$ (IIb)	174—174,5 (2,3)	1,5108	0,9657	89,72	88,59	78,41	11,01	4,90	—	78,84	4,84
$C_8H_5CH_2O-CH=CH-C\equiv C-CH_2-N(C_2H_5)_2$ (IIc)	159(3)	1,5345	0,9786	77,36	75,54	78,57	11,12	4,77	—	78,97	5,76
Iodomethyl derivatives (IIlc)	M.P.	—	—	—	—	79,04	8,85	—	—	—	—
	83—83,5					52,76	6,31	—	—	52,99	—
						52,63	6,29	—	—	6,27	32,93

ture was stirred for four hours and allowed to stand over night. The thick reaction mixture was treated with an aqueous solution of ammonium chloride until two layers appeared. The upper layer, after drying over sodium sulfate and removal of the solvent, was distilled in vacuo. Obtained: fraction I, b.p. 35 - 45° (3 mm); 1.2 g; fraction II, b.p. 122 - 126° (3 mm); 11.7 g; residue - 3.8 g.

Fraction I consisted of original unreacted materials. Fraction II consisted of 1, 1-diethylxy-5-butoxypentene-4-yne-2 (Ia) or of the diethyl acetal of butoxybutenylal, b.p. 133° (4mm); n_D^{20} 1.4698; d_4^{20} 0.9422; found MR 66.61; calculated for $C_{13}H_{22}O_3$ Δ MR 63.53; yield 70.0% of theoretical. In similar fashion 1, 1-diethoxy-5-phenylethoxypentene-4-yne-2 (Ib), 1, 1-diethoxy-5-thioethylpentene-4-yne-2 (IVa) and 1, 1-diethoxy-5-thiobutylpentene-4-yne-2 (IVb) were prepared from ethynylvinylphenylethyl, ethynylvinylthioethyl and ethynylvinylthiobutyl ethers. The yields, constants and analytical results are shown in Table 1.

TABLE 3

Original substance	Found, % of theoret.	
	thioether acetal	ethylmercaptan curochlo ride
$C_2H_5S-CH=CH-C\equiv C-CH(OC_2H_5)_2$	97,34 97,79	99,0 100,0
$C_4H_9S-CH=CH-C\equiv C-CH(OC_2H_5)_2$	— —	99,8 99,1

Hydrogenation of 1, 1-diethoxy-5-phenylethoxybutene-4-yne-2. 3.2g of the diethyl acetal of phenylethoxybutenylal were hydrogenated over platinum oxide at room temperature (according to Adams). In the course of 11 hours, 820 ml of hydrogen were consumed. 0.9 g (28.1% of theoretical) of 1, 1-diethoxy-5-phenylethoxypentadiene-2,4 (Va) were obtained by fractional distillation; b.p. 117 - 117.5° (3 mm); n_D^{20} 1.5043; d_4^{20} 1.0004; found MR 81.15; calculated for $C_{17}H_{24}O_3$ Δ MR 81.10. Found: C 74.01, 73.88; H 8.73, 8.68%. $C_{17}H_{24}O_3$. Calculated: C 73.88; H 8.75%. 0.7 g (30.4% of theoret.) of 1, 1-diethoxy-5-phenylethoxypentane (VIa), b.p. 128° (3 mm), n_D^{20} 1.4858 were also obtained. Found: C 72.57, 72.82; H 9.44, 9.62%. $C_{17}H_{22}O_3$. Calculated: C 72.81; H 10.00%.

Decomposition of thioetheracetals by an alcoholic solution of mercuric chloride. The decomposition was carried out by the method described in [8]. The results of the experiment are shown in Table 3.

Preparation of Mannich bases from ethynylvinyl ethers (equation 3). In a flask supplied with a stirrer, thermometer and reflux condenser, were placed 6.7 g (0.054 M) of freshly distilled ethynylvinylbutyl ether, 2.1 g (0.07 M) of paraformaldehyde, 5.4 g (0.07 M) of diethylamine and 8 ml of ethyl alcohol. The reaction mixture was stirred and heated to boiling (82°) for five hours. After cooling, the mixture was fractionally distilled and 2 g of the original ethynylvinylbutyl ether b.p. 55° (9 mm) were recovered and 5.1 g of a substance that was found to be 1-butoxy-5-diethyl-aminopentene-1-yne-3 (IIa). Its yield was 64.6% of theoret.; b.p. 130 - 130.5° (8 mm); n_D^{20} 1.4782; d_4^{20} 0.8854; found MR 66.92; calculated for $C_{13}H_{23}ON$ MR 64.69. Found: C 74.58, 74.30; H 11.22, 11.17; N 7.06, 7.18%. $C_{13}H_{23}ON$, calculated: C 74.53; H 11.16; N 6.69%.

Preparation of the iodomethyl derivative of the base. 0.8 g of the Mannich base were mixed with an ether solution of 0.6 g of methyl iodide while the mixture was cooled with ice water and stirred. The solution, which had become turbid, was heated to boiling for one hour. Colorless crystals of the iodomethyl derivative (IIIa) deposited from the lower oily layer on standing which, after being twice recrystallized from an ether solution of ethyl alcohol had a m.p. of 75 - 75.5°. Found: C 47.98, 47.80; H 7.20, 7.34; N 36.34, 36.21%. $C_{14}H_{26}ON$, calculated: C 47.78; H 7.46; N 36.12%.

In a similar manner the corresponding bases were obtained from ethynylvinyl- β -decalyl and ethynylvinylbenzyl ethers: 1- β -decaloxy-5-diethylaminopentene-1-yne-3 (IIb) with a yield of 56.6% and also their iodomethyl derivatives (IIIb) and (IIIc). Their constants and analytical data are shown in Table 2. The iodomethyl derivative of decahydroxydiethylaminopentene (IIb) was separated as an uncrystallizable oil.

SUMMARY

1. The conditions for the reaction of thioethylvinyl ethers with the ethyl ester of orthoformic acid by means of the organo-magnesium complex were studied.
2. A series of new etheracetals and thioetheracetals containing a pentenyne chain of carbon atoms was synthesized. Trialkoxypentadienes-1, 3 and saturated etheracetals, not previously described, were obtained. Ethynylvinylphenylethyl ether was also synthesized.

3. New Mannich bases were synthesized by the reaction of ethynylvinyl ethers with paraformaldehyde and diethylamine, and iodomethyl derivatives of them were obtained.

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STUDIES OF LACTONES AND LACTAMS

REPORT 19. THE SYNTHESIS OF ETHERS AND ESTERS OF N-(β -HYDROXYETHYL) PYRROLIDONE

M. F. Shostakovskii, F. P. Sidel'kovskaya and M. G. Zelenskaya

Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

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Nauk, 1961, No. 5,

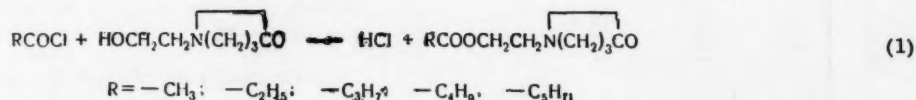
pp. 910-913, May, 1961

Original article submitted April 20, 1960

On the basis of data in the literature and materials prepared by the authors, it is possible to draw the conclusion that the presence of the lactam ring in compounds causes an increase in their solubility, in their solvent power and in their tendency to form complexes, which in a number of cases is of great interest.

The formation of esters of carboxylic acids by means of N-(β -hydroxyethyl) pyrrolidone was studied for the purpose of finding methods of introducing the lactam ring into the structure of organic compounds. The esters of N-(β -hydroxyethyl) pyrrolidone and saturated monobasic acids have not been described. The reaction of acid chlorides with aminoalcohols is recommended in the literature for the synthesis of esters on the basis of aminoalcohols and fatty acids [1].

We obtained esters with a yield of 90 - 95 % by the action of N-(β -hydroxyethyl) pyrrolidone on the chlorides of acetic, propionic, butyric, valerianic, and caproic acids.



It was found that in order to get a good yield of the esters it is necessary to use a small excess of acid chloride (0.2 - 0.3 M) in comparison with N-(β -hydroxyethyl) pyrrolidone since purification of the esters from contamination by unreacted N-(β -hydroxyethyl) pyrrolidone is very difficult. The synthesized esters are colorless, odorless liquids, soluble in water, ether, alcohol, and benzene (the ester of caproic acid is almost insoluble in water). Physical constants and analytical data are shown in Table 1.

TABLE 1. Physical Constants of Esters of N-(β -Hydroxyethyl)pyrrolidone and Fatty Acids.

R	B.p. °C (pressure in mm)	n_D^{20}	d_4^{20}	MR		Found			Calculated		
				found	calculated	C	H	N	C	H	N
H	131-132(1,5)	1,4795	1,1780	37,87	37,93	53,70 53,88	6,92 6,96	9,29 9,27	53,49	6,92	8,91
CH ₃	163-164(2,5)	1,4720	1,1301	42,42	42,54	56,43 56,40	7,53 7,56	8,20 8,48	56,13	7,65	8,18
C ₂ H ₅	147-149(1,5)	1,4708	1,1017	46,99	47,17	58,11 57,82	8,02 8,20	7,96 7,72	58,35	8,16	7,56
n-C ₃ H ₇	162-163(1,5)	1,4708	1,0799	51,55	51,78	60,08 59,90	8,56 8,74	6,79 6,77	60,28	8,60	7,03
n-C ₄ H ₉	167-168(1,5)	1,4676	1,0527	56,16	56,40	61,83 62,10	9,08 9,15	6,95 6,87	61,94	8,98	6,56
n-C ₅ H ₁₁	180-182(1,5)	1,4668	1,0330	61,03	61,02	63,06 62,90	9,22 9,31	6,44 6,19	63,41	9,31	6,16

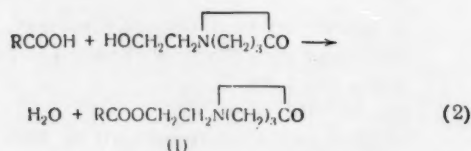
TABLE 2. Physical Properties of β, β -di-(N-2-hydroxypolymethyleneimino) diethyl Ethers

Ether	Yield of ether, %	B.p. °C (pressure in mm)	n_D^{20}	d_4^{20}	MR		Mol. wt.		Found, %			Calculated, %		
					found	calculated	found	calculated	C	H	N	C	H	N
β, β' -di-(No-2-oxotrimethyleneimino)-diethyl ether	46	124-130 (2, 2-10 ⁻²)	1,5070	1,1432	62,76	62,55	236,4	240,31	59,77	8,25	11,24	59,97	8,39	11,66
β, β' -di-(No-2-oxotetramethyleneimino) diethyl ether	29	125-130 (2, 8-10 ⁻²)	1,5040	1,1091	71,64	71,99	249,4	268,39	59,77	8,44	11,75			10,44
β, β' -di-(No-2-oxopentamethyleneimino) diethyl ether	23	130-140 (1, 8-10 ⁻²)	1,5022	1,0875	80,75	81,23	275,8	296,4	64,08	9,79	8,68	64,83	9,52	9,45

• Literature data [6]: B.p. 200° (1.5 · 10⁻¹ mm).

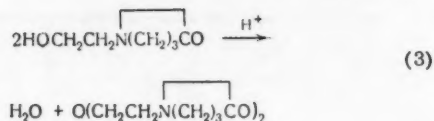
With increasing molecular weight of the esters the index of refraction and the specific gravity decrease. The molecular refraction of the esters is somewhat lower (by 0.2 - 0.3) than the theoretically calculated figure.

It was of interest to examine the possibility of using the direct esterification reaction for the synthesis of the esters mentioned above.

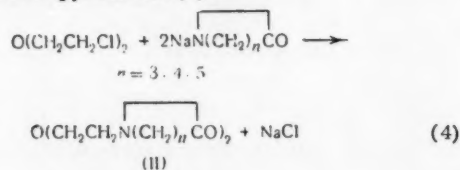


The esters of formic, acetic and valeric acids were prepared by means of this reaction with an 80% yield. The best yields were obtained when the ratio of the original components was 3 M of acid per 1 M of N-(β -hydroxyethyl) pyrrolidone, with a process temperature of 80° and a reaction time of 6-12 hours. When equimolecular quantities of the original reactants were used, the yield decreased to 40% even when the process was continued for 20-25 days. The direct esterification process offers some advantages since it makes possible the preparation of esters in one step and the yields of the final products are close (the yield of esters when acid chlorides react with N-(β -hydroxyethyl) pyrrolidone calculated on the basis of the original acid, amount to 70%, while the yield of esters prepared by direct esterification is ~80%).

On distillation of esters (1), prepared by direct esterification, the formation of insignificant quantities of viscous residues was observed. As a result of repeated distillation of these residues, collected from a number of experiments, a product was obtained that appeared to be an ester, namely β, β' -di-(N-2-hydroxymethyleneimino) diethyl ester (II n = 3). The latter was formed, apparently, owing to the esterification of N-(β -hydroxyethyl) pyrrolidone by the separation of water under the influence of concentrated sulfuric acid.



In order to prove the structure of this compound, it was prepared by independent synthesis from β, β' -dichlorodiethyl ether and sodium pyrrolidone (4)



Inasmuch as ethers with lactam rings are of independent interest, we synthesized analogous compounds according to reaction (4) on the basis of sodium piperidone and sodium caprolactam. Ethers of structure (II) are viscous liquids with a slight yellow color. As the molecular weight increases, the yield of ethers decreases. They are soluble in water, alcohol, acetone and benzene and are insoluble in ether and in petroleum ether. The physical properties and analyses of the ethers are shown in Table 2.

EXPERIMENTAL

N-(β -hydroxyethyl) pyrrolidone was prepared by reacting monoethanolamine with γ -butyrolactone [2] or by the combination of pyrrolidone with ethylene oxide [3]. The acid chlorides were synthesized in the usual manner from acids and thionyl chloride [4].

The Preparation of Esters of Saturated Acids and N-(β -Hydroxyethyl) Pyrrolidone

Esterification reaction. A mixture of 0.15 M N-(β -hydroxyethyl) pyrrolidone, 0.45 M of acid, 0.2 ml of concentrated sulfuric acid and 60 ml of absolute benzene were boiled under a reflux condenser. The water that separated was collected in a Dean and Stark receptacle. The length of the boiling was determined by the quantity of water that separated; it amounted to from 6 - 12 hours. Benzene was first distilled from the reaction mixture at a pressure of 60-80 mm, and then the acid at 20 - 30 mm. The residue was distilled at 1 - 2 mm yielding the ester with a yield of ~ 80%. In order to purify it, the ester was repeatedly distilled through a column with 30 theoretical plates. The physical constants and analyses of these esters are shown in Table 1.

The reaction of acid chlorides with N-(β -hydroxyethyl) pyrrolidone. A mixture of 0.15 M of acid chlorides and 0.13 M of N-(β -hydroxyethyl) pyrrolidone in 80 ml of absolute benzene was boiled for eight hours. The reaction mixture was neutralized with a saturated soda solution. The benzene layer was separated from the aqueous layer, and the latter was extracted with ether. The benzene layer and the ether extract were dried over sodium sulfate. Then the ether and benzene were distilled off at 60 - 80 mm and the residue was distilled at 1 - 2 mm. This gave the ester that we were seeking which was redistilled twice through a column of 30 theoretical plates. The yield was 85 - 90%.

Synthesis of Ethers Containing Lactam Rings.

Reaction of β , β -dichlorodiethyl ether with sodium lactams. A lactam salt was prepared from 0.1 M of metallic sodium and 0.1 M of lactam in 35 ml of xylene according to the method previously described [5]. To the salt obtained, 0.05 M of β , β' -dichlorodiethyl ether were added through a dropping funnel, with energetic stirring, during the course of 30 minutes. The reaction mixture was boiled at 135-138°. A precipitate of sodium chloride was filtered off and washed with ether. The ether and xylene were distilled off at 30-50 mm, and the viscous residue was distilled at 10⁻² mm. The physical constants and analyses of the ethers synthesized are shown in Table 2.

SUMMARY

1. The esters of saturated acids (formic, acetic, propionic, butyric, valerianic and caproic) and N-(β -hydroxyethyl) pyrrolidone were synthesized by the reaction of the latter with the acid chlorides of the acids mentioned, and also by direct esterification.
2. By the reaction of β , β' -dichlorodiethyl ether with sodium lactams, ethers containing lactam rings were prepared: β , β' -di-(N-2-oxotrimethyleneimino) diethyl ether, β , β' -di-(2-oxotetramethyleneimino) diethylether and β , β' -di-(N-2-oxopentamethyleneimino) diethyl ether.

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BRIEF COMMUNICATIONS

THE COMBINATION OF NITRILE CHLORIDE WITH ACRYLIC AND METHACRYLIC ACIDS AND THEIR DERIVATIVES

S. S. Novikov, G. A. Shvekhgeimer and N. F. Pyatakov

Zelinskii Institute of Organic Chemistry, Academy of Sciences SSSR

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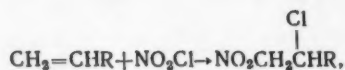
Original article submitted August 15, 1960

Previously Shechter and his co-workers [1] combined nitrile chloride with acrylic acid and with its methyl ester and nitrile and obtained α -chloro- β -nitropropionic acid, and also its methyl ester and nitrile.

In order to study this reaction more thoroughly we repeated the experiments of Shechter and his co-workers and also further studied this reaction using as examples the chloroanhydride of acrylic acid, methacrylic acid, and its methyl ester and chloroanhydride under comparable conditions without intermediate separation of nitrile chloride.

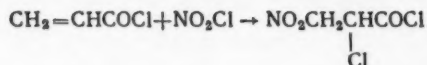
This method of carrying out the reaction decreases the yields of dinitrohalogen compounds, but it considerably simplifies the process.

The reaction products of nitrile chloride with acrylic acid, with its methyl ester and with its nitrile have identical yields (65-67%).



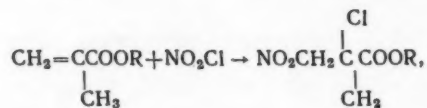
where R = COOH, COOCH₃, CN.

A higher yield of the product (81%) was obtained by the reaction of the chloroanhydride of acrylic acid with nitrile chloride



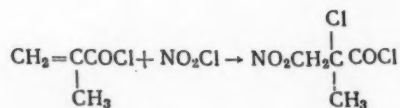
It should be noted that the chloroanhydride of α -chloro- β -nitroacrylic acid which forms undergoes saponification to the acid very quickly and easily in the presence of the moisture of the air.

The combination of nitrile chloride with methacrylic acid and with its methyl ester occurs only with considerable effort, and the yields of the combination products are lower, 49 and 32% respectively.



where R = H, CH₃.

In the case of the chloroanhydride of methacrylic acid the yield of the combination product is somewhat higher - 62%.



EXPERIMENTAL

Nitrile chloride was prepared according to the method of Shechter and his co-workers [1]. A steady stream of nitrile chloride was passed through a safety flask and into the reaction mixture. The temperature of the reaction was maintained within the assigned interval by the rate of flow of nitrile chloride through the mixture, and by external cooling (with ice and salt). In the case of acrylic and methacrylic acids the reaction was conducted in a solution of chloroform; in the remaining cases the nitrile chloride was passed directly into the unsaturated compound.

The combination of nitrile chloride with acrylic acid. Nitrile chloride, formed by the gradual addition of 47 ml (87 g, 0.7 M) of chlorosulfonic acid to a mixture of 30 ml of nitric acid ($d = 1.5$) and 30 ml of 30% oleum, was introduced, with stirring, into a solution of 36 g (0.5 M) of freshly distilled acrylic acid in 20 ml of dry chloroform for two hours at 0–5°. After passing in the NO_2Cl the mixture was stirred for 30 minutes at 0–5°; the mixture was allowed to warm up to room temperature and the excess of nitrile chloride was blown out by a current of nitrogen while the mixture was stirred. The chloroform was evaporated by heating the mixture under the vacuum of a water pump.

49.5 g (65%) of α -chloro- β -nitropropionic acid were obtained; m.p. 77–79° (from benzene). The literature [1] gives m.p. 78–80°.

The combination of nitrile chloride with methacrylic acid. During a two hour period, with stirring, and at 0–5°, nitrile chloride formed from 0.7 M of nitric acid ($d = 1.5$) and 0.7 M of chlorosulfonic acid in the presence of 30% oleum, was passed into a solution of 43 g (0.5 M) of freshly distilled methacrylic acid in 20 ml of dry chloroform. This was stirred for a further 30 minutes at 0–5° and then allowed to warm up to room temperature, after which the excess of nitrile chloride was blown out with a current of nitrogen. This resulted in the formation of a crystalline precipitate of the combination product (29.5 g). The liquid phase was evaporated and crystals separated out.

Altogether 41 g (49) of α -methyl- α -chloro- β -nitropropionic acid, m.p. 86–88° (from a 1 : 2 mixture of benzene–cyclohexane), were obtained. Found: C 29.12, 29.02; H 3.61, 3.65; Cl 21.29, 21.27%. $\text{C}_4\text{H}_6\text{NO}_4\text{Cl}$. Calculated: C 28.69; H 3.59; Cl 20.95%.

The combination of nitrile chloride with the chloroanhydride of acrylic acid. During a period of 3.5 hours at 0–5° and with stirring, nitrile chloride formed from 1.2 M of nitric acid ($d = 1.5$) and 1.2 M of chlorosulfonic acid in the presence of 30% oleum, was passed into 90 g (1 M) of the freshly distilled anhydride of acrylic acid. After introducing the nitrile chloride, the mixture was stirred for 30 minutes at 0–5°, allowed to warm up to room temperature, and the excess nitrile chloride removed in a current of nitrogen. There remained 139 g (81%) of the product of combination which was left in the air for one to two days for complete saponification to the acid.

129 g of α -chloro- β -nitropropionic acid were obtained. The combination product from the other experiment, carried out under conditions that prevented it from reacting with the moisture of the air, was distilled in a current of dry nitrogen; the chloroanhydride of α -chloro- β -nitropropionic acid was obtained; b.p. 97–98° (8 mm); n_D^{20} 1.4850; n_D^{20} 1.5466. Found: C 21.05, 21.08; H 1.87, 1.93; Cl 41.38, 41.10%. $\text{C}_3\text{H}_3\text{NO}_2\text{Cl}_2$. Calculated: C 20.93; H 1.80; Cl 41.28%.

The remaining experiments were carried out in similar fashion and the following products obtained:

1. From the methyl ester of acrylic acid—the methyl ester of α -chloro- β -nitropropionic acid; yield 67%, b.p. 70–110° (3–4 mm); on repeated distillation the majority of the product distilled at 86–88° (4 mm). The literature [1] shows: b.p. 68–110° (2–4 mm).

2. From acrylonitrile—the nitrile of α -chloro- β -nitropropionic acid, yield 67%; b.p. 86–95° (2 mm); on repeated distillation the majority of it distilled at 88–90° (1 mm). The literature gives [1]: b.p. 88–91° (1–1.5 mm).

3. From the methyl ester of methacrylic acid—the methyl ester of α -methyl- α -chloro- β -nitropropionic acid, yield 32%; b.p. 95–115° (9 mm); on repeated distillation the majority of it distilled at 103–106° (8 mm); n_D^{20} 1.4540; d_4^{20} 1.2565. Found: C 33.31, 33.27; H 4.63, 4.71; Cl 19.29, 18.96%. $\text{C}_5\text{H}_8\text{NO}_4\text{Cl}$. Calculated: C 33.06; H 4.41; Cl 19.55%.

4. From the chloroanhydride of methacrylic acid—the chloroanhydride of α -methyl- α -chloro- β -nitropropionic acid, yield 62%; b.p. 75–90° (2–5 mm); on repeated distillation the majority of it distilled at 78–81° (1 mm); n_D^{20} 1.4782; d_4^{20} 1.4232. Found: C 25.86, 25.70; H 2.97, 2.97; Cl 37.96, 38.02%. $\text{C}_4\text{H}_5\text{NO}_3\text{Cl}_2$. Calculated: C 25.81; H 2.69; Cl 38.71%.

SUMMARY

1. The reactions of nitrile chloride with acrylic and methacrylic acids and their derivatives were studied.
2. The combination products of nitrile chloride with the chloroanhydrides of acrylic and methacrylic acids and with methacrylic acid and its methyl ester were prepared and characterized for the first time.

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THE SYNTHESIS OF ESTERS OF ALKYLTHIOBORIC ACIDS FROM TRIALKYLBORON AND THIOBORATES

B. M. Mikhailov, T. A. Shchegoleva and E. M. Shashkova

Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

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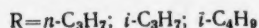
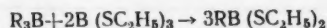
Nauk, 1961, No. 5,

pp. 916-917, May, 1961

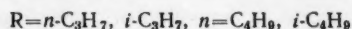
Original article submitted October 3, 1960

The esters of alkylthioboric acids are synthesized by reacting alkylborondihalogenides (chlorides or bromides) with mercaptans [1, 2]. This type of compound may also be obtained by combining tetra-(*n*-butylmercapto) diborane [3] or tri-(ethylmercapto) diborane [4] with olefins, as well as by the action of mercaptans on complex compounds of alkylboranes with triethylamine [5]. The dimethyl ester of methylthioboric acid is formed by slowly heating methylthioborate and the methyl ester of dimethylthioboric acid which, in turn, is prepared from methylthioborate and trimethylboron in the presence of diborane [6].

We found that the esters of alkylthioboric acids may be prepared directly from trialkylboron and thioborate. On heating a mixture of trialkylboron and ethylthioborate (in a ratio of 1 : 2) for 30 - 35 hours at $\sim 250^\circ$, the ethyl ester of alkylthioboric acid is formed with a yield of 65 - 75%.

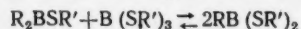
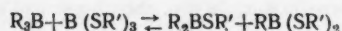


The ethyl esters of *n*-propyl, isopropyl- and isobutylthioboric acids were synthesized in this way. The reaction of trialkylborons with *n*-butylthioborate, under the same conditions, proceeds somewhat less easily.



The yields of the butyl esters of alkylthioboric acids amount to only 50%. Moreover the reaction products contain a certain quantity (10 - 15%) of the ester of dialkylthioboric acid, and also some unchanged trialkylboron and butylthioborate.

The formation of the esters of alkylthioboric acids by the reaction of trialkylboron and thioborate is a process which is the opposite of the process of symmetrization which is very common in the chemistry of organo-boron compounds. Apparently an equilibrium exists between these two processes.



In the case of ethylthioborate, the equilibrium is considerably displaced toward the right because the ethyl esters of alkylthioboric acids are sufficiently thermally stable. The butyl esters of alkylthioboric acids, according to our studies, are more inclined toward symmetrization, which explains the more complicated composition of the reaction products.

EXPERIMENTAL

The diethyl ester of *n*-propylthioboric acid. A mixture of 6.9 g (0.05 M) of tri-*n*-propylboron and 19.4 g (0.10 M) of ethylthioborate [4] was placed in a two necked flask with an inlet for nitrogen and a reflux condenser. It was boiled on a metal bath for 35 hours. On subsequent distillation the following fractions were obtained: I. 49-65°

(3 mm); 2.4 g; II. 67–69° (3 mm), 17.8 g; III. 70–90° (3 mm), 3.4 g. Fraction II was the diethyl ester of n-propylthioboric acid. The yield was 67.4%; d_4^{20} 0.9299; n_D^{20} 1.4987; MR 55.59 found; MR 56.05 calculated. Found: S 36.44; 36.31; B 6.65, 6.69%. $C_7H_{17}BS_2$. Calculated: S 36.40; B 6.14%.

The diethyl esters of isopropylthioboric and isobutylthioboric acids. The reactions of triethylthioborate with triisopropylboron or triisobutylboron were carried out similarly to that described above. The yields and physical properties of the diethyl esters of isopropylthioboric and isobutylthioboric acids are shown in Table 1.

The di-n-butyl ester of isobutylthioboric acid. A mixture of 6.8 g (0.037 M) of triisobutylboron and 20.8 g (0.075 M) of tri-n-butylthioborate [7] was heated on a metal bath at 240–250° for 30 hours. On distillation the following fractions were obtained: I. 60–90° (1 mm), 2.2 g; II. 90–115° (1 mm), 1.4 g; III. 117–120° (1 mm), 14.2 g; IV. 125–150° (1 mm), 2.5 g; V. 150–155° (1 mm), 4.5 g. Fraction I contained a mixture of the original triisobutylthioboron and the n-butyl ester of diisobutylthioboric acid; fraction II was the n-butyl ester of diisobutylthioboric acid; n_D^{20} 1.4520; data from the literature: b.p. 107° (9.5 mm); n_D^{20} 1.4572; fraction III was the di-n-butyl ester of isobutylthioboric acid, yield 52.5%; n_D^{20} 1.4902; data from the literature [3]: b.p. 141–142° (3.5 mm); n_D^{20} 1.4919; fraction V was n-butylthioborate; n_D^{20} 1.5190; data from the literature [7]: b.p. 150–152° (1 mm); n_D^{20} 1.5205.

TABLE 1

RB(SC ₂ H ₅) ₂	Yield, %	B.p. °C (press. in mm)	d_4^{20}	n_D^{20}	MR		Found, %		Calculated, %	
					found	calculated	S	B	S	B
i-C ₃ H ₇ B(SC ₂ H ₅) ₂	69	63–64(2)	0.9303	1.4963	55.34	56.05	36.31	36.27	6.40	6.36
i-C ₄ H ₉ B(SC ₂ H ₅) ₂	76	83–84(2)	0.9099	1.4888	60.30	60.70	34.06	33.97	6.23	6.10

TABLE 2

RB(SC ₄ H ₉) ₂	Yield	B.p. °C (press. in mm)	n_D^{20}	Literature data	
				b.p. °C (press. in mm)	n_D^{20}
n-C ₃ H ₇ B(SC ₄ H ₉) ₂	52	122–125(2)	1.4940	150(13)	1.4956[1]
n-C ₄ H ₉ B(SC ₄ H ₉) ₂	54	115–120(1)	1.4920	148–150(7)	1.4936[1]
i-C ₃ H ₇ B(SC ₄ H ₉) ₂	47	117–122(1)	1.4920	128–129(7)	1.4960[2]

The di-n-butyl esters of n-propylthioboric, isopropylthioboric and n-butylthioboric acids. The reactions of n-butylthioborate with tri-n-propyl, triisopropyl and tri-n-butylboron were carried out similarly. The yields of the di-n-butyl esters of the alkylthioboric acids and some of their physical properties are shown in Table 2.

The symmetrization of the di-n-butyl ester of isobutylthioboric acid. 12.5 g (0.05 M) of the di-n-butyl ester of isobutylthioboric acid was heated for 10 hours at a temperature of 240–250°. On subsequent fractional distillation in vacuo the following fractions were obtained: I. 1.3 g (0.006 M) of the n-butyl ester of di-isobutylthioboric acid; b.p. 80–90° (1 mm); n_D^{20} 1.4534; II. 7.8 g (0.03 M) of the original ester, b.p. 122–125° (1 mm), n_D^{20} 1.4911; III. 2.3 g (0.008 M) of n-butylthioborate, b.p. 150–155° (1 mm), n_D^{20} 1.5162.

Thus, under the conditions of the experiment, 30% of the di-n-butyl ester of isobutylthioboric acid symmetrized.

SUMMARY

The esters of alkylthioboric acids are obtained by heating trialkylboron with trialkylthioborates.

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REACTIONS OF TRIETHYLBORATE WITH AMINES

T. A. Shchegoleva, E. M. Shashkova and B. M. Mikhailov

Zelinskii Institute of Organic Chemistry, Academy of Sciences USSR

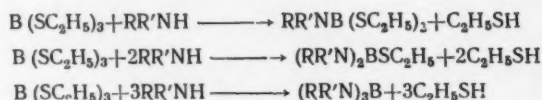
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The convenient method which we proposed for the synthesis of esters of thioboric acids by the reaction of di-borane with mercaptans [1, 2] makes it possible to study this type of boron compound. The present paper gives the results of studies of the conversion of thioborates under the influence of amines. We found that when primary or secondary aliphatic amines act on triethylthioborate, a consecutive replacement of the alkylmercaptan groups by the corresponding alkylamino groups occurs and, as a result, N-substituted di-(alkylmercapto) aminoboron, alkylmercaptodiaminoboron or triaminoboron is formed, depending on the reagent ratio.

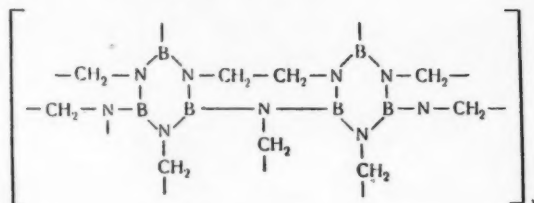


Di-(ethylmercapto) ethylaminoboron, di-(ethylmercapto) dimethylaminoboron, ethylmercapto-di-ethylaminoboron, ethylmercapto-di-(dimethylamino) boron and tri-(n-butylamino) boron were synthesized in this way. They are colorless liquids which may be distilled in vacuo without noticeable decomposition.

Di-(ethylmercapto) phenylaminoboron, formed by the action of one equivalent of aniline on ethylthioborate, easily symmetrizes. Even at room temperature it is slowly converted to tri-(phenylamino) boron and ethylthioborate. Heating considerably accelerates this change; therefore efforts to distill this compound yielded only products of its disproportionation. With pyridine, triethylthioborate gives a complex which is also a liquid. On heating, the pyridine decomposes into the original components.

The reaction of ethylthioborate with ethylenediamine proceeds in an interesting way when the ratios of the reactants are 1 : 1. A polymer containing ~ 20% of boron and no ethylmercapto groups is formed. In this case, apparently, all the hydrogens attached to nitrogen are replaced by boron, while all the mercapto groups on the boron are replaced by amino groups.

We suggest that the polymer has the following structure:



EXPERIMENTAL

Di-(ethylmercapto) ethylaminoboron. 2.5 g (0.06 M) of ethylamine were added to 11.0 g (0.06 M) of ethylthioborate at room temperature. During the addition the mixture warmed up. Under the vacuum of a water pump, the ethylmercaptan formed was distilled off into a receptacle cooled to -70° (4.2 ml, 97.5% of theoretical calculated on the basis of one alkylmercapto group). The residue was then distilled. 5.8 g (58% of theoret.) of di-(ethyl-

mercapto) ethylaminoboron were obtained. B.p. 51–54° (0.07 mm); d_4^{20} 0.9744; n_D^{20} 1.5122; MR 54.57 found; MR 54.94 calculated. Found: C 40.89; H 9.12; B 6.53%. $C_6H_{16}BNS_2$. Calculated: C 40.68; H 9.10; B 6.11%.

Di-(ethylmercapto) dimethylaminoboron. In a similar manner, 6.9 g (49% of theoret.) of di-(ethylmercapto) dimethylaminoboron were obtained from 15.5 g (0.08 M) of ethylthioborate and 3.6 g (0.08 M) of dimethylamine; b.p. 68–72° (1 mm); d_4^{20} 0.9826; n_D^{20} 1.5147; MR 54.34 found; MR 55.11 calculated. Found: C 40.77, 41.03; H 9.35; 9.61%. $C_6H_{16}BNS_2$. Calculated: C 40.68; H 9.10%.

Ethylmercapto-di-(ethylamino) boron. 10.8 g (0.24 M) of ethylamine were added to 23.3 g (0.12 M) of ethylthioborate at room temperature; the reaction mixture warmed up. After removal of the ethylmercaptan in vacuum (17.0 ml, 95% of theoretical calculated on two alkylmercapto groups) the residue was distilled. 10.2 g (52% of theoret.) of ethylmercapto-di-(ethylamino) boron with a b.p. of 75–80° (3 mm) were obtained. On repeated distillation the substance had a b.p. of 73–76° (3 mm); d_4^{20} 0.9219; n_D^{20} 1.4805; MR 49.38 found; MR 49.89 calculated. Found: C 45.12, 45.08; H 10.47, 10.70%. $C_6H_{17}BN_2S$. Calculated: C 45.01; H 10.70%.

Ethylmercapto-di-(dimethylamino) boron. 4.6 g (35%) of ethylmercapto-di-(di-methylamino) boron were prepared in a similar manner from 15.5 g (0.08 M) of ethylthioborate and 7.2 g (0.16 M) of dimethylamine. The product had a b.p. of 52–55° (1 mm); d_4^{20} 0.9037; n_D^{20} 1.4822; MR 50.52 found; MR 50.26 calculated. Found: C 45.18, 45.48; H 10.69, 10.62%. $C_6H_{17}BN_2S$. Calculated: C 45.01; H 10.70%. In addition, 5.0 g (35% of theoret.) of di-(ethylmercapto) dimethylaminoboron, b.p. 68–78° (1 mm), were obtained.

Tri-(n-butylamino) boron. 10.2 g (0.14 M) of n-butylamine were added to 9.0 g (0.046 M) of ethylthioborate at room temperature; the reaction mixture heated up. 10.0 ml (93.5% of theoret calculated on three ethylmercapto groups) of ethylmercaptan were distilled off under the vacuum of a water pump, and the residue was distilled. 5.9 g (57% of theoret.) of tri-n-butylaminoboron were obtained; b.p. 100–102° (0.06 mm); d_4^{20} 0.8378; d_D^{20} 1.4482, MR 72.63 found, MR 72.76 calculated. The literature shows [3]; b.p. 84 (0.005 mm); d_4^{20} 0.8347; n_D^{20} 1.4462.

Di-(ethylmercapto) phenylaminoboron. 11.3 g (0.122 M) of aniline were added to 23.7 g (0.122 M) of ethylthioborate at room temperature during which the mixture heated up. The liquid remaining after removal the ethylmercaptan under a vacuum was di-(ethylmercapto) phenylaminoboron; d_4^{20} 1.07733; n_D^{20} 1.5882, MR 70.37 found, MR 71.12 calculated. Found: B 5.28, 5.29%. $C_{10}H_{16}BNS_2$. Calculated: B 4.80%. At room temperature the substance gradually symmetrizes. After prolonged standing the precipitate of tri-(phenylamino) boron which formed was filtered off and washed with hexane. 7.8 g were obtained; m.p. 163–167°. The literature shows [4]; m.p. 170°. On distilling the filtrate, 5.8 g of ethylthioborate were obtained; b.p. 87–90° (1 mm), n_D^{20} 1.5440. The literature gives [2]; b.p. 86–87° (1 mm); n_D^{20} 1.5465. Di-(ethylmercapto) phenylaminoboron rapidly symmetrizes on heating and therefore it is not possible to distill it.

The pyridinate of triethylthioborate. On adding 3.2 g (0.04 M) of pyridine to 7.7 g (0.04 M) of ethylthioborate the reaction mixture warms up and takes on an orange color. The complex which is formed is stable at room temperature (the pyridine did not distill off under a 2 mm vacuum); d_4^{20} 1.1098; n_D^{20} 1.5872. On distillation 6.5 g of ethylthioborate were obtained; b.p. 60–63° (0.05 mm), n_D^{20} 1.5443. On cooling a trap to –70°, 2.0 g of pyridine condensed; n_D^{20} 1.5050.

The action of ethylenediamine on triethylthioborate. To a solution of 16.3 g (0.08 M) of ethylthioborate in 10 ml of dioxane, cooled to 0°, was added a solution of 5.0 g (0.08 M) of ethylenediamine in 5 ml of dioxane, whereupon a small precipitate formed at once. The ethylmercaptan and dioxane were removed under the vacuum of a water pump. The residue (6.5 g) was a white solid which was not soluble in ether, benzene or hexane. It quickly deliquesced in air; was hydrolyzed by cold water; and was easily soluble in methyl alcohol. It did not melt up to 250°, but it began to change at 180°. Found: B 18.29, 19.79%. $(C_9H_{18}B_6N_9)X$. Calculated: B 20.46%.

SUMMARY

1. Primary and secondary amines react with thioborates to form N-substituted di-(alkylmercapto) aminoboron, alkylmercaptodiaminoboron and triaminoboron.
2. With tertiary amines the thioborates form complex compounds.

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THE INFLUENCE OF THE SILYL GROUP ON THE RATE
OF DEHYDROCHLORINATION OF SOME β AND γ -
CHLOROALKYLSILANE CHLORIDES

V. F. Mironov and V. V. Nepomnina

N. D. Zelinskii Institute of Organic Chemistry

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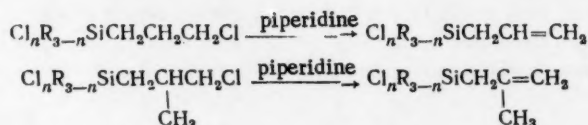
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In the preceding papers [1, 2] we determined that the ease of detaching hydrogen chloride from haloalkylsilanes by the action of quinoline is independent of the nature of the silyl group and depends on the position of the chlorine atom in relation to a silicon atom, as follows: $\gamma < \alpha < \beta$.

γ -Chloroalkylsilane chlorides showed practically no detachment of hydrogen chloride by the action of quinoline. We found later, however, [2, 3] that it is possible to bring about the dehydrochlorination of γ -chloroalkylsilane chlorides by the use of piperidine, which results in the formation of a series of alkenylsilanes with good yields [3]:



The use of piperidine for the dehydrochlorination of some β -chloroalkylsilane chloride unexpectedly showed that the latter detach HCl considerably less readily than γ -chloroalkylsilane chlorides.

For the purpose of evaluating piperidine as a dehydrochlorinating agent and determining the limits of its applicability, in the present study we undertook to investigate the relative activity of a series of α -, β - and γ -chloroalkylsilane chlorides in their reaction with piperidine. The dehydrochlorination of these chloroalkylsilane chlorides

Compound No.	Formula	Quantity, M	Products obtained	% of substance obtained
1	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0,2	$\text{Cl}_3\text{SiCH}_2\text{CH}=\text{CH}_2$	30
2	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0,2	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}=\text{CH}_2$	70
	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0,3	$\text{Cl}_3\text{SiCH}_2\text{CH}=\text{CH}_2$	38
	$(\text{CH}_3)_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0,3	$(\text{CH}_3)_3\text{SiCH}_2\text{CH}=\text{CH}_2$	0
3	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{Cl}$	0,3	$\text{Cl}_3\text{SiCH}=\text{CH}_2$	80
	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{Cl}$	0,3	$\text{CH}_3\text{Cl}_2\text{SiCH}=\text{CH}_2$	20
4	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{Cl}$	0,3	$\text{CH}_3\text{Cl}_2\text{SiCH}=\text{CH}_2$	33
	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0,3	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}=\text{CH}_2$	86
5	$\text{CH}_3\text{Cl}_2\text{SiCHClCH}_3$	0,2	$\text{CH}_3\text{Cl}_2\text{SiCH}=\text{CH}_2$	0
	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0,2	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}=\text{CH}_2$	73
6	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{Cl}$	0,3	$\text{Cl}_3\text{SiCH}=\text{CH}_2$	47,9
	$\text{Cl}_3\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0,3	$\text{Cl}_3\text{SiCH}_2\text{CH}=\text{CH}_2$	24,5
7	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}_2\text{CH}_2\text{Cl}$	0,2	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\text{CH}=\text{CH}_2$	55,1
	$\text{CH}_3\text{Cl}_2\text{SiCH}_2\underset{\text{CH}_3}{\text{CHCH}_2\text{Cl}}$	0,2	$\text{CH}_3\text{Cl}_2\text{SiCH}_2-\underset{\text{CH}_3}{\text{C}}=\text{CH}_2$	41,5

by catalytic quantities of piperidine gives identically high yields, but the reaction time for one and the same compound varies because the induction time before the reaction begins is non-constant and hard to evaluate. In this connection we decided to evaluate the ease of detaching HCl from chloroalkylsilane chlorides by the so-called "Mutual competition" reaction. The detachment of hydrogen chloride by the action of piperidine was carried out simultaneously in a mixture of two comparable chloroalkylsilyl chlorides in equimolecular quantities. By comparing the quantity of alkenylsilanes formed during different intervals of time, it would be possible to draw a conclusion concerning the greater or lesser ease of detachment of HCl from one of the chloroalkylsilane chlorides that were being compared. The table shows the results of the dehydrochlorination of seven pairs of chloroalkylsilane chlorides that were compared.

In pairs 1 and 2 we succeeded in establishing that, for compounds with the chlorine atom in the γ -position relative to silicon, the ease of dehydrochlorination increases in the following order, depending on the nature of the silyl group $(CH_3)_3Si < Cl_3Si < CH_3Cl_2Si$. For compounds with the chlorine atom in the β -position (pair 3), however, the ease of detachment of HCl bears a reverse relationship to the nature of the silyl group: $CH_3Cl_2Si < Cl_3Si$, and corresponds with the rule previously observed by us [1] for compounds of the type $Cl_nR_{3-n}SiCH_2CH_2Cl$, for which the ease of detachment of HCl by the action of quinoline increased as n increased. This is apparently connected with the reciprocal effect of the silyl group with the β -chlorine atom (σ - σ -linking, which increases as n decreases. It is easy to see from the results of the dehydrochlorination of pairs 4 and 5, that the ease of detachment of HCl is determined by the location of the chlorine atom relative to silicon and shows the following relationship: $\alpha < \beta < \gamma$. It is essential to note, however, that this dependence is only valid for compounds with the CH_3Cl_2Si group. In the presence of the Cl_3Si group the relationship is reversed, i.e. $\gamma < \beta$ (pair 6). Thus it became clear that the ease of detachment of HCl and the formation of the corresponding silico-olefins by the action of catalytic quantities of piperidine on haloalkylsilane chlorides is determined, not so much by the location of the chlorine atom relative to the silicon atom, as by the nature of the silyl group. The differences noted between β and γ -chloroalkylsilane chlorides in dehydrochlorination reactions are probably explained by the fact that these compounds detach HCl by the action of organic bases by various mechanisms, depending on the nature of the silyl group. And, finally, the results of the dehydrochlorination of the seventh pair of compounds showed that they had practically identical activity in the dehydrochlorination reaction.

EXPERIMENTAL

The dehydrochlorination of a mixture of $CH_3Cl_2SiCH_2CH_2CH_2Cl$ and $CH_3Cl_2SiCH_2CH_2CH_2Cl$. From a 200 ml flask equipped with a column and a descending condenser, a mixture of 53.3 g (0.3 M) of $CH_3Cl_2SiCH_2CH_2CH_2Cl$, 57.4 g (0.3 M) of $CH_3Cl_2SiCH_2CH_2CH_2Cl$ and 2.5 g of piperidine were slowly distilled at a temperature of not above 150°. By a single distillation through a column of three portions of the condensate, a total of 13 g of $CH_3Cl_2SiCH=CH_2$ (bp. 92°; yield 33%) and 45 g of $CH_3Cl_2SiCH_2CH=CH_2$ (b.p. 117°; yield 86%) were obtained.

The dehydrochlorination of a mixture of $CH_3Cl_2SiCH_2CH_2CH_2Cl$ and $Cl_3SiCH_2CH_2CH_2Cl$. In a similar manner a mixture consisting of 42 g (0.2 M) of $Cl_3SiCH_2CH_2CH_2Cl$, 38 g (0.2 M) of $CH_3Cl_2SiCH_2CH_2CH_2Cl$ and 2.1 g of piperidine were dehydrochlorinated. A fraction with a b.p. of 115–118° was obtained by distilling through a column. By titrating three portions of the condensate, selected at different times, with 0.1 N NaOH, a mixture of 30% of $Cl_3SiCH_2CH=CH_2$ and 70% of $CH_3Cl_2SiCH_2CH=CH_2$ was found. Spectral analysis of this mixture (KRS spectra) gave approximately the same ratio. Experiments with other pairs of compounds were carried out similarly (see table).

SUMMARY

1. The nature of the silyl group plays a decisive role in influencing the ease of dehydrochlorination of β - and γ -chloroalkylsilane chlorides by piperidine.

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THE NATURE OF THE BRANCHING OF THE POLAROGRAPHIC WAVE OF ALBUMINS IN SOLUTIONS OF COBALT SALTS

S. G. Mairanovskii and E. F. Mairanovskaya

N. D. Zelinskii Institute of Organic Chemistry, Acad. Sci. USSR,
and the Hertsen State Oncological Institute, Ministry of Health
of the Russian Soviet Federative Socialist Republic
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The present study was undertaken for the purpose of elucidating the nature of the branching of the widely known polarographic protein curve of Brdicka in solutions of cobalt salts (see, for example [1]). The shape of the catalytic protein wave testifies to the "surface" character of at least one of its steps, i.e., it indicates that the catalytically active substance is found in the adsorbed state and that the chemical reactions, preceding electron transfer, do not proceed in the bulk of the solution, but instead they take place on the surface of the electrode [2, 3].

To determine the character of the albumin steps we investigated the effect of the electrode dropping time on their height, selecting as the subject of study the wave of the sulfosalicylic acid filtrate of blood serum in ammoniacal buffer, containing hexammine cobalt (III). The experiments were run using a special dropping electrode, fitted with a small blade for the forced removal of the drops, which blade could be operated by means of a microscrew. In this manner, with a practically constant mercury flow rate ($m = 0.69$ mg/sec), we were able to vary the dropping time t within fairly wide limits.

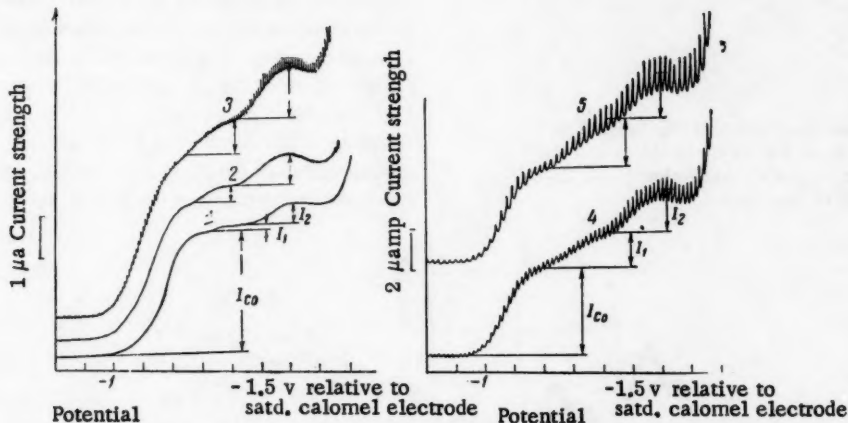


Fig. 1. Samples of polarograms of sulfosalicylic acid filtrate of blood serum (according to Brdicka) in ammoniacal buffer containing $\text{Co}(\text{NH}_3)_3\text{Cl}_3$ at different t :

1 - 0.36; 2 - 0.75; 3 - 1.5; 4 - 2.8; 5 - 3.6 sec.

Samples of the polarograms taken by us of the same solution at different t of the dropping electrode are shown in Fig. 1. With decrease in t the first albumin step diminishes much more rapidly than does the second. The relationship between the logarithm of the heights of the steps and $\log t$ is shown in Fig. 2. This relationship is linear for all of the steps.

For the diffusion wave of cobalt (straight line 1, Fig. 2) the slope of the straight line $\log i_{\text{diffusion}}$ vs. $\log t$, as

was to be expected [4], lies close to 0.18. The slope of the straight line for the first albumin step (line 2) lies close to $7/6$, i.e., this step increases proportionally to $t^{7/6}$. An increase in the current, proportional to $t^{7/6}$, is apparently determined by an increase in the surface concentration of the adsorbed catalyst, when the process of catalyst adsorption (preceding for a long time prior to the advent of adsorption equilibrium) is limited by diffusion [5], in which connection the catalyst is either weakly adsorbed or its concentration in the solution is very small [5]. The slope of straight line 3, Fig. 2, is equal to $2/3$, and this indicates either a surface character for the 2nd albumin wave, with a nearly established adsorption equilibrium of the catalyst, or a bulk process [2]; in both of these cases the current is proportional only to the value of the electrode surface. The assumption that the 2nd wave has a bulk nature is contradictory to the experimental data. Thus, if it is assumed, by analogy with the waves of quinine [2], that the 2nd wave is produced by the same catalyst as the 1st wave, but operating in the bulk of the solution, then the presence of higher aliphatic acids, chemically reacting with the catalyst [6], would reduce both of the waves to the same degree. Actually, only the 2nd wave decreases here [6]. As a result, both of the waves apparently have a surface character.

The different character of the adsorption processes, relating to the 1st and 2nd protein steps, testifies to the fact that the catalytically active groups producing them do not belong to the same albumin molecule. In other words, two catalysts are present in the solution, differing in their properties. The catalyst of the 1st albumin wave is more weakly adsorbed than the catalyst of the 2nd wave, and consequently under the influence of surface-active gelatin the height of the 1st step decreases, while that of the 2nd remains almost unchanged (see, for example, Fig. 4 in the paper by Marha [6]; the heights of the waves were determined by us using the method schematically shown in Fig. 3 of the given paper); this is evidenced by the smaller temperature coefficient of the 1st wave [7], if it is assumed that the activation energies of the chemical processes, determining the heights of the two waves, are close. The presence of two types of catalyst cannot be attributed to the presence of different albumin molecules in the solution, since a double wave is also observed for individual albumins in solutions of cobalt salts. The appearance of two waves is probably associated with the formation of several types of Co complexes (apparently, II) with the albumin molecule,

differing in either composition or structure and heterodynamic in their catalytic properties. Abundant data testify to the greater stability of the complex of the 1st wave. The concentration of the Co^{2+} ions in the solution exerts a different influence on the height of the albumin waves, i.e., it exerts a different influence on the formation of the corresponding catalytic complexes. The polarograms taken from Brdicka's paper [8] are shown in Fig. 3, and in the upper right-hand corner of Fig. 3 we have shown the curves constructed by us for the relationship between the heights of the individual waves and the concentration of CoCl_2 in the solution. The height of the second albumin maximum was read by us from the level of

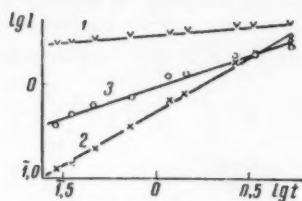


Fig. 2. Relationship between the heights of the individual steps of the albumin wave and the dropping time: 1) of cobalt wave; 2) of 1st albumin step; 3) of 2nd step.

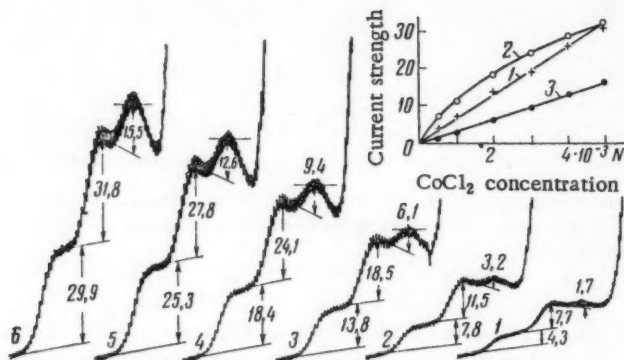


Fig. 3. Polarograms of blood serum in 0.1N NH_4Cl and 0.1N NH_4OH at different CoCl_2 concentrations (in 10^{-3}N): 1) 0.5; 2) 1.0; 3) 2.0; 4) 3.0; 5) 4.0; 6) 5.0 (from Brdicka's paper [8]). The designations on the waves are ours. The heights of the waves as a function of the CoCl_2 concentration are plotted in the upper right-hand corner: 1) limiting current of the Co^{2+} wave; 2) maximum current of the 1st albumin step; 3) the same for the 2nd step.

the linearly extrapolated current of the descent of the 1st albumin wave (see Fig. 3). To read the 2nd maximum it would be more correct to find the true continuation of the 1st wave [3], but for purposes of comparison the accuracy of the method of reading used by us is quite adequate. From Fig. 3 it follows that the height of the 2nd maximum increases linearly with the CoCl_2 concentration, whereas the growth of the 1st maximum gradually slows down.

It is interesting that the 2nd wave is the first to decrease when ethylenediaminetetraacetic acid (EDTA) is added to the Brdicka solution (see Fig. 4 in [9]). This is easily explained by the fact that EDTA, tying up the Co^{2+} ions, reduces their concentration in the solution, in which connection the relationship between the heights of the waves and the concentration of the remaining Co^{2+} ions in the solution is approximately the same as that shown in Fig. 3.

A disappearance of the catalytic wave when the Co^{2+} ions are tied up by a complexing agent was also observed by Brezina [10].

If the solution contains a complexing agent that combines with cobalt more strongly than the latter is combined in the catalyst of the 2nd wave, but weaker than in the catalyst of the 1st wave, then only the 1st albumin wave should remain on the polarograms. Such a phenomenon was actually observed by Ito [11], who worked with a solution of tris-(ethylenediamine) cobalt chloride.

The influence of various chemical factors, changing the height of albumin waves, for example, the effect of the higher aliphatic acids [6] or of formaldehyde [12], can be explained either by a blocking of the catalytically active centers or a tying up of the groups participating in the formation of the complex, or by a change in the adsorbability of one of the catalysts.

SUMMARY

1. The reason for the branching of the albumin wave in the presence of cobalt salts is because at least two catalytically active complexes of the albumin with Co^{2+} ions, differing in both catalytic and adsorption properties, are present in the solution.
2. The influence of various factors on the separate steps of the albumin wave was explained by the dissimilar action of these factors on each of the catalytic complexes.

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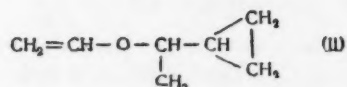
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POLYMERIZATION OF THE VINYL ETHER OF METHYLCYCLOPROPYLCARBINOL

M. F. Shostakovskii, E. P. Gracheva, A. P. Meshcheryakov,
and V. G. Glukhovtsev

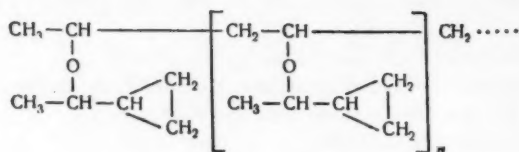
N. D. Zelinskii Institute of Organic Chemistry, Acad. Sci. USSR.
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Previously [1] we had described a large number of vinyl ethers of the following general structure: $\text{CH}_2 = \text{CHOR}$ (I), where R is an alkyl, aryl, naphyl or aralkyl radical. Here it was established that the double bond in these compounds exhibits a high nucleophilicity, which becomes especially manifest in various addition reactions, transformations, and partly in the polymerization reaction. In connection with studying the conditions for the polymerization of compounds (I), especial interest is possessed by the vinyl ether of methylcyclopropylcarbinol.

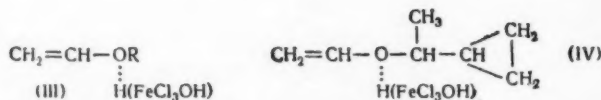


The cyclopropyl group of this ether is potentially a carrier of the properties of the propenyl radical and can add various polar compounds, in harmony with the Markovnikov rule. In addition, the vinyl ether of methylcyclopropylcarbinol possesses interest in connection with studying its behavior in both polymerization and copolymerization reactions for the purpose of obtaining various polymers, including graft polymers.

In this paper we describe the polymerization of the vinyl ether of methylcyclopropylcarbinol in the presence of the initiators FeCl_3 and azobisisobutyronitrile, under the conditions considered to be optimum for the polymerization of vinyl alkyl ethers. In the course of our work we established that the reactivity of compound (II) when polymerized in the presence of 5% FeCl_3 solution (in dioxane) is higher than that of the vinyl alkyl ethers (I). This higher reactivity is most clearly evident in that the polymerization of ether (II) begins at 0° and the highest yield of polymer is obtained at -17 to -20° , whereas the vinyl alkyl ethers are polymerized only at their respective boiling points [2]. The scheme for the formation of the polymer of ether (II) can be depicted in the following manner:



We regard the reason for such a difference in the polymerization temperatures to be due to the difference in the stability of the oxonium complexes of these compounds (I, II).



Complex (IV) is the less stable of the two complexes, and its decomposition begins at a low temperature, which leads to formation of the polymer at a lower temperature. We were unable to effect the polymerization of this ether (II) using an initiator capable of inducing free-radical reactions (azobisisobutyronitrile).

EXPERIMENTAL

The vinyl ether of methylcyclopropylcarbinol was synthesized by the Favorskii-Shostakovskii method, starting with methylcyclopropylcarbinol and acetylene in the presence of potassium hydroxide [3]. The ether had the following constants: b.p. 115° (756 mm); n_D^{20} 1.4284; d_4^{20} 0.8392. The isolation of the obtained polymers in the pure state was accomplished by dissolving them in ether or acetone, followed by precipitation with methyl alcohol. After removal of most of the solvent and methyl alcohol by decantation, the precipitated polymer was dried for 4-5 hr at 50-60° in vacuo (20 mm) for the purpose of removing residual impurities. An Ostwald viscosimeter was used to determine the viscosity (in centipoises) of a solution of 1 g of the polymer in 100 ml of benzene at 20°. A three-necked flask, fitted with a stirrer, reflux condenser and thermometer, was used to run the polymerization of vinyl ether (II) in the presence of 3-4 drops of 5% FeCl₃ solution (in dioxane).

The charge placed in the flask was 0.11-0.16 mole of unsaturated ether, which was cooled to -17 to -20°, and then about 0.03-0.06 g of catalyst solution was added with constant stirring. Here it was observed that the reaction mixture became thick and the temperature rose 5-15°. After this the temperature of the mixture dropped slowly and after approximately an hour it reached the initial reaction temperature (-17 to -20°). At this stage the reaction was stopped.

Polymerization of vinyl ether of methylcyclopropylcarbinol using 5% FeCl₃ solution (in dioxane). The polymerization of 11.3 g of the ether in the presence of 3-4 drops of the catalyst gave 8.7 g (77%) of slightly yellow viscous polymer, which after purification had: viscosity η_{20} 0.4236; 0.4241 centipoises; n_D^{20} 1.4783; molecular 876.9; 917; 1110. Found: C 74.48, 74.52; H 10.63, 10.50%. Calculated: C 74.85; H 10.7%. The polymer is soluble in benzene, n-heptane, acetone, ether and dioxane, and is insoluble in the alcohols: methyl, ethyl, butyl, etc.

Polymerization of vinyl ether of methylcyclopropylcarbinol using azobisisobutyronitrile. A mixture of 20 g of the ether and 0.1 g of the crystalline catalyst was placed in a sealed ampul and heated in a thermostat for 100 hr at 60°. After this, the ampul contents were distilled (atmospheric pressure); here we recovered 18.8 g (97%) of the starting ether, while the catalyst crystallized on the sides of the flask. The slightly yellow liquid remaining in the distillation flask was dissolved in ether and then methyl alcohol was added to precipitate the polymer. The solution remained clear.

SUMMARY

1. Conditions were found for the polymerization of the vinyl ether of methylcyclopropylcarbinol using FeCl₃ catalyst (5% solution in dioxane), and the obtained polymer was characterized.
2. The polymerization of the vinyl ether of methylcyclopropylcarbinol does not go in the presence of azobisisobutyronitrile.

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REGULATING THE SPECIFICITY OF THE HOMOGENEITY OF CELLULOSE BY MEANS OF TEMPERATURE IN THE PROCESS OF TREATMENT WITH DILUTE NITRIC ACID

B. A. Zakharov, V. I. Ivanov, A. L. Mal'tseva,
and G. A. Krylova

N. D. Zelinskii Institute of Organic Chemistry, Acad. Sci. USSR
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Previously we had shown [1-3] that the high values of the physicochemical properties of cellulose fibers and papers are determined mainly by the homogeneity of the cellulose in the finished products along the length of the chain molecules. Chemical methods of homogenization were also established by us [4, 5]. As had already been mentioned, to obtain a complex of the physicochemical properties of various cellulose products it is important to have a specific coupling of two characteristics of homogeneity: the degree of homogeneity and the specificity of homogeneity. The first characteristic determines the amount of predominant molecules, while the second characteristic determines their average molecular weight.

In the case of the homogenization of cellulose with dilute nitric acid [4] three factors influence the process: concentration of the acid, temperature, and length of treatment. In our investigations we found that the concentration of the acid and the time control the degree of homogeneity to a certain extent, whereas regulating the specificity of homogeneity is achieved by varying the temperature of treatment.

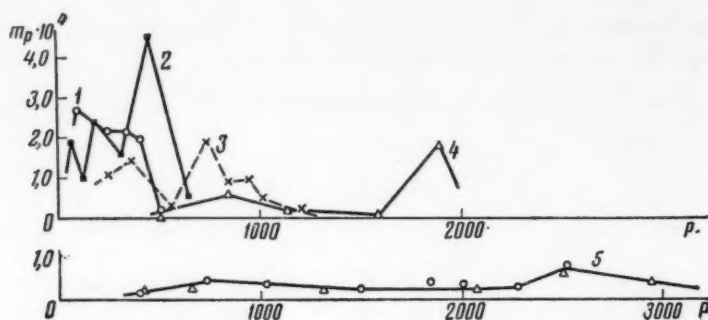


Fig. 1. Effect of temperature and time on the homogenization of cellulose with 0.2N HNO_3 : 1) 99°, 30 min; 2) 92°, 1 hr; 3) 70°, 2 hr; 4) 50°, 3 hr; 5) starting standard cotton cellulose; p) degree of polymerization.

As a result of this we discovered a way of obtaining homogeneous celluloses, naturally with the requirement that the conditions for retaining homogeneity will be adopted in the production process. High values for the specificity of homogeneity determine the correct coupling of the strength and elastic properties of the products (fibers, papers).

Standard cotton cellulose, prepared by the Corey and Gray method, was subjected to homogenization with 0.2N nitric acid; this cellulose was extremely heterogeneous along the length of the chain molecules; its molecular-weight distribution is characterized by Curve 5. In this connection the two kinds of points relate to two different fractions made two years apart. The molecular-weight distribution curves for the homogenized cellulose samples relate to the following temperature and time conditions of treatment with nitric acid: 1) 99°, 30 min; 2) 92°, 1 hr; 3) 70°.

2 hr; 4) 50°, 3 hr. As can be seen from Fig. 1, reducing the temperature (from 99°) and increasing the length of treatment (from 30 min to 3 hr) make it possible to obtain an assembly of celluloses with a variable value for the specificity of homogeneity, in which connection the degree of polymerization of the predominant fraction shifts from 100 to 1900.

SUMMARY

1. A study was made of the use of nitric acid to homogenize cellulose along the length of the chain molecules and to vary the specificity of homogeneity.
2. It was established that it is possible to change the specificity of cellulose homogeneity by varying the temperature and time of the homogenization process.

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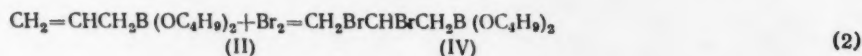
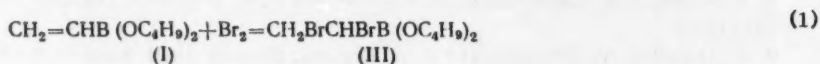
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β - DECOMPOSITION OF BUTYL ESTERS OF α , β -DI BROMOETHYLBORONIC AND β , γ -DIBROMOPROPYLBORONIC ACIDS

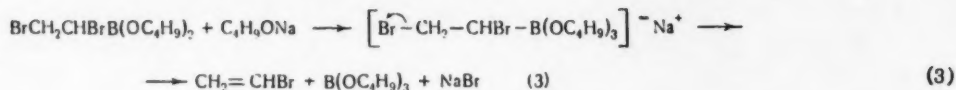
B. M. Mikhailov and P. M. Aronovich

N. D. Zelinskii Institute of Organic Chemistry, Acad. Sci. USSR
Translated from *Izvestiya Akademii Nauk SSSR, Otd. Khimicheskikh
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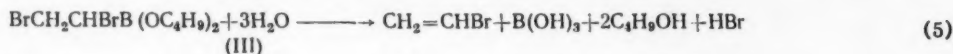
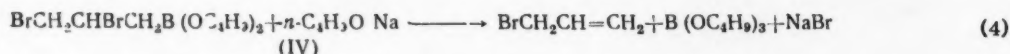
Continuing our earlier [1, 2] study of the properties of the esters of unsaturated organoboron acids, we accomplished the addition of bromine to the di-n-butyl esters of vinyl- (I) and allylboronic (II) acids, and in this way obtained the di-n-butyl esters of α , β -dibromoethylboronic (III) and β , γ -dibromopropylboronic (IV) acids.



The unsaturated bromide is liberated when esters (III) and (IV) are treated with an alcoholic solution of alcoholate or with dilute acid or alkali solution. As a result, the esters of the dibromoethyl- and dibromopropylboronic acids undergo β -decomposition when treated with nucleophilic reagents. Taking into consideration the tendency displayed by organoboron compounds to form complexes, it is possible to assume that esters (III) and (IV) first form complexes with the reagent, after which the bromine (found in the β -position) is cleaved as negative ion and the B-C bond is ruptured. For example, the reaction of the dibromoethylboronic ester with alcoholate can be expressed by the scheme:

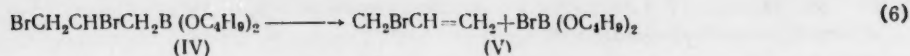


The following reactions probably also proceed by a similar mechanism:



According to Equation (5), half of the bromine contained in esters (III) and (IV) is determined by titration with silver nitrate solution.

Ester (IV), in which the bromine atoms are found in the β , γ -positions with respect to the boron atom, decomposes more easily than does ester (III), where the bromine atoms are in the α - β -positions. Thus, the latter remains unchanged after 6-hour heating at 140-150°, whereas the β , γ -dibromopropylboronic ester decomposes partially even when distilled, forming tributyl borate, allyl bromide and butyl bromide. The primary product of the cleavage of ester (IV), besides allyl bromide, is probably the dibutyl ester of the bromoboronic acid (V), which decomposes further, according to the data of Bujwid, Gerrard and Lappert [3], to butyl bromide, tributyl borate and boric anhydride.



It should be mentioned that the decomposition of organoboron compounds, containing halogen in the β -position, was observed earlier for $(\text{ClCH}=\text{CH})_2\text{BOH}$, $\text{ClCH}=\text{CHB}=\text{CHB}(\text{OH})_2$ [4] and $\text{ClCH}_2\text{CH}_2\text{BCl}_2 \cdot \text{O}(\text{CH}_3)_2$ [5].

EXPERIMENTAL

Di-n-butyl ester of α, β -dibromoethylboronic acid (III). To a stirred mixture of 25.2 g (0.137 mole) of di-n-butyl vinylboronate [6] in 25 ml of n-hexane was added at -20 to -30° , in 20 min, 22.6 g (0.141 mole) of bromine, diluted with 15 ml of n-hexane. Then the mixture was stirred for 1 hr without cooling, the hexane and excess bromine were removed by vacuum-distillation, and the residue was distilled to give 44 g (93.5%) of the di-n-butyl ester of α, β -dibromoethylboronic acid with $142-143^\circ$ (3 mm): d_4^{20} 1.3391; d_D^{20} 1.4730. Found: C 35.09, 35.28; H 5.94, 6.22; B 3.29, 2.94; Br 46.18, 46.03%. $\text{C}_{10}\text{H}_{21}\text{O}_2\text{BBr}_2$. Calculated: C 34.92; H 6.15; B 3.17; Br 46.47%.

Di-n-butyl ester of β - γ -dibromopropylboronic acid (IV). Using the same conditions as above, 17.7 g (0.107 mole) of bromine was added to 20.6 g (0.104 mole) of the di-n-butyl ester of allylboronic acid [7]. On rapid distillation from a Claisen flask we obtained 4.1 g of mixed tributyl borate and di-n-butyl β, γ -dibromopropylboronate, b.p. $72-117^\circ$ (0.4 mm), and 28.6 g (77%) of the dibutyl ester of β, γ -dibromopropylboronic acid, b.p. $117-124^\circ$ (0.4 mm), and n_D^{20} 1.4747. When redistilled, the ester had b.p. $126-128^\circ$ (0.5 mm); d_4^{20} 1.3337; d_D^{20} 1.4755. Found: C 37.24, 37.25; H 6.43, 6.67; B 3.17, 3.25; Br 44.53, 44.32%. $\text{C}_{11}\text{H}_{23}\text{O}_2\text{BBr}_2$. Calculated: C 36.90; H 6.48; B 3.02; Br 44.66%. Ester (IV) fumes strongly in the air. When 20 g of the ester was distilled through a short fractionating column at 6 mm we collected two fractions: fraction I, 11.2 g, b.p. $80-137^\circ$ (6 mm), and fraction II, 7.1 g of ester (IV) contaminated with tributyl borate, b.p. $137-140^\circ$ (6 mm); n_D^{20} 1.4568. Redistillation of fraction I gave tributyl borate with b.p. $87-90^\circ$ (6 mm); n_D^{20} 1.4112. Literature data [8]: b.p. $105-106^\circ$ (8 mm); n_D^{20} 1.4080. During the distillation of ester (IV) we collected 3.2 g of liquid in the traps, from which we were unable to isolate any pure substances by distillation. After adding a solution of bromine in isopentane to the mixture, followed by distillation, we obtained 0.8 g of n-C₄H₉Br, b.p. $96-99^\circ$; n_D^{20} 1.4420 (literature data [9]: b.p. 101.6° ; n_D^{20} 1.4398), and 3.25 g of 1, 2, 3-tribromopropane, b.p. $111-115^\circ$ (32 mm); n_D^{20} 1.5795 (literature data [10]: b.p. 102° (18 mm); n_D^{20} 1.5863). Consequently, the original mixture contained 1.4 g of allyl bromide.

Reaction of sodium butylate with the di-n-butyl ester of α, β -dibromoethylboronic acid. To 17.2 g (0.05 mole) of the dibutyl ester of α, β -dibromoethylboronic acid was added with stirring, in 20-30 min, a solution of sodium n-butylate in butyl alcohol, prepared from 1.15 g (0.05 mole) of sodium and 30 ml of absolute n-butyl alcohol. The reaction was exothermic, and the temperature of the mixture was held at $15-20^\circ$ by cooling with water. The mixture of liquid and precipitate was stirred for 2.5 hr at room temperature, after which the vinyl bromide was distilled at room temperature and 200 mm of pressure. In the traps (cooled to -70°) we collected 3.2 g (60%) of vinyl bromide, which vaporized completely at room temperature (22°); n_D^{12} 1.4335. Literature data [11]: b.p. 15.8° ; n_D^{20} 1.4462. After removal of the vinyl bromide by distillation the reaction mixture was filtered, and the precipitate was washed with benzene and dried. We obtained 5.0 g (97%) of NaBr. Distillation of the filtrate gave 9.4 g (81.7%) of tributyl borate with b.p. $82-86^\circ$ (4 mm); n_D^{20} 1.4105.

Reaction of sodium butylate with the di-n-butyl ester of β, γ -dibromopropylboronic acid. Using the same conditions as above, 15 g (0.042 mole) of the di-n-butyl ester of β, γ -dibromopropylboronic acid was reacted with 0.043 mole of sodium butylate in butanol, after which the precipitate (the volatile products were condensed in the cold traps) was filtered and washed with isopentane. The yield of sodium bromide was 4.2 g (97.5%). Distillation of the filtrate gave a mixture of allyl bromide and butanol, b.p. $32-58^\circ$ (180 mm), and tri-n-butyl borate, 8.8 g (91%), b.p. $98-102^\circ$ (8 mm); n_D^{20} 1.4095. Distillation of the 1st fraction and the contents of the traps through a short column gave 3.24 g (64%) of allyl bromide with b.p. $68-74^\circ$; n_D^{20} 1.4612. Literature data [12]: b.p. 70° (759 mm); n_D^{20} 1.4697.

Action of 0.1 N sulfuric acid solution on the di-n-butyl ester of α, β -dibromoethylboronic acid. To a mixture of 23.5 g (0.068 mole) of the dibutyl ester of α, β -dibromoethylboronic acid and 20 ml of diethyl ether was added with stirring, at room temperature, in 10 min, 4 ml (0.222 mole of water) of 0.1 N sulfuric acid solution. After several minutes a precipitate began to deposit. The mixture was stirred for 4 hr at room temperature, and the precipitate was filtered, washed with ether, and dried in vacuo. We obtained 1.55 g of boric acid. The filtrate contained 5.15 g (0.0635 mole) of hydrogen bromide. Distillation of the filtrate gave: 1) 0.9 g of n-butanol with b.p.

35–38° (14 mm); n_D^{20} 1.4002; 2) 5.2 g of tributyl borate with b.p. 81–88° (4 mm); n_D^{20} 1.4145; and 3) 1.5 g of the dibutyl dibromoethylboronate with b.p. 132–139° (3 mm); n_D^{20} 1.4695. The yield of boric acid (as such and as the tributyl ester), based on reacted ester (II), was 74.7% of the theoretical. All of the operations were carried out in an atmosphere of dry nitrogen.

SUMMARY

1. The dibutyl esters of the vinyl- and allylboronic acids add bromine smoothly.
2. The dibutyl esters of α , β -dibromoethylboronic acid and β , γ -dibromopropylboronic acid easily undergo β -decomposition.

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THE HYDROLYTIC CLEAVAGE OF D'-METHOXY-D-(HYDROXYMETHYL) DIETHYLENE GLYCOL IN ACID MEDIUM

Z. I. Kuznetsova and V. I. Ivanov

N. D. Zelinskii Institute of Organic Chemistry, Acad. Sci. USSR

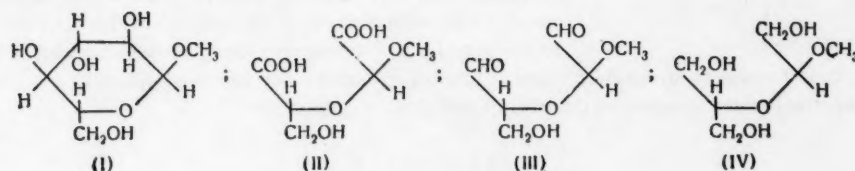
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Using the method of comparative hydrolysis, it was shown in our previous papers [1, 2] that opening the pyran ring in α -methylglucoside (I), with the formation of either COOH (II) or CHO (III) groups at C₂ and C₄, leads to the formation of compounds with an acetal linkage that is less stable in acid medium than the corresponding linkage in α -methylglucoside.



From the work of Smith and Van Cleve [3] it follows that D'-methoxy-D-(hydroxymethyl) diethylene glycol (IV) is also unstable in acid medium (its optical activity is lost completely when treated with 1 N hydrochloric acid for 15 min at room temperature).

Our data on studying the hydrolysis rate of D'-methoxy-D-(hydroxymethyl) diethylene glycol (IV) in 1 N hydrochloric acid at various temperatures (20, 11, and 5°) are given in the present paper. It was found that in 1 N hydrochloric acid compound (IV) is hydrolyzed completely in 20 min at 20°; here the hydrolysis rate constant is of the order of $3.69 \times 10^{-3} \text{ sec}^{-1}$. The hydrolysis rate constants of compound (IV) at lower temperatures are given in Table 1.

TABLE 1. Hydrolysis of D'-Methoxy-D-(hydroxymethyl) diethylene Glycol in 1N Hydrochloric Acid at 11 and 5°

Hydrolysis time, seconds	At 11°		At 5°	
	Extent of hydrolysis, %	$k \cdot 10^{-3} \text{ sec}^{-1}$	Extent of hydrolysis, %	$k \cdot 10^{-3} \text{ sec}^{-1}$
82	10,54	1,358		
120	14,54	1,309		
300	33,00	1,336		
600	—	—	37,50	0,792
720	55,92	1,094	—	—
1200	—	—	51,29	0,600
1800			55,22	0,447
2400			58,48	0,366
3000			67,78	0,377
Average		1,274	Average 0,516	

* Hydrolysis rate constant.

From the data in Tables 1 and 2 it follows that the rate constants for the hydrolysis of D'-methoxy-D-(hydroxymethyl) diethylene glycol (IV) in 1N hydrochloric acid at 11 and 5° are of the same order as the rate constant for the hydrolysis (in 1N HCl) of D'-methoxy-D-(hydroxymethyl) diglycolic acid (II) at 80°. As a result, based on the hydrolysis rate in 1N hydrochloric acid, compounds (I)-(IV) fall into the following order: (IV) > (II) > (III) > (I). Proceeding from the mechanism for the hydrolysis of these compounds in acid medium, which was discussed by us in a previous paper [2], we correlate such an order in the ease of hydrolysis with the electronegativity of the functional groups at C₂ and C₄, and also with the electronegativity of the pyran ring as a whole. We regard the earlier studied compounds (II) and (III) as model compounds for oxidized celluloses, having anhydroglucose moieties in the macromolecule with COOH and CHO groups at C₂ and C₃. Anhydroglucose units of type (II) and (III) can exist not only in oxidized celluloses, but also in samples of so-called native cellulose. The existence of anhydroglucose moieties

of type (IV) in the macromolecule of native and oxidized cellulose is hardly probable, but their properties represent substantial interest for reduced oxycelluloses. From the above discussed data it can be seen that the existence of anhydroglucose moieties with three CH₂OH groups in the macromolecule of modified cellulose should lead to a sharp reduction in the stability of the acetal linkage (in the α-position to the CH₂OH group) in acid medium.

In studies made both in our laboratory [4] and elsewhere [5, 6], on the example of modified celluloses, containing fragments (II)-(IV), analogous data were obtained relative to the hydrolysis rates of the compounds by mineral acids in heterogeneous medium. The data obtained on the hydrolysis of the corresponding model compounds, i.e., compounds

TABLE 2. Hydrolysis Rate Constants of Compounds (I), (II) and (III) in 1N Hydrochloric Acid at 80 and 60°

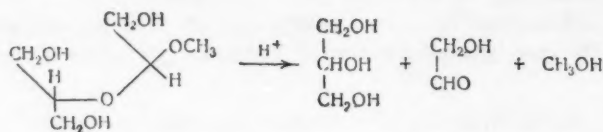
Compound	Hydrolysis rate constant, sec ⁻¹	
	at 80°	at 60°
II	1,410·10 ⁻³	2,270·10 ⁻⁴
III	1,970·10 ⁻⁴	4,050·10 ⁻⁵
I	2,46·10 ⁻⁵	2,860·10 ⁻⁶

(I)-(IV), by acids in homogeneous medium make it possible to remove any possible objections relative to the influence of the supermolecular structure in the case of modified celluloses

EXPERIMENTAL

D'-Methoxy-D-(hydroxymethyl) diethylene glycol (IV) was obtained by the reduction of D'-methoxy-D-(hydroxymethyl) diglycolaldehyde (III) with sodium borohydride in alkaline medium [7]. It had the following constants: n_D^{25} 1.4690. Found: C 43.20, 43.03; H 8.32, 8.35%. C₆H₁₄O₅. Calculated: C 43.4; H 8.40%.

The hydrolysis of compound (IV) went in accordance with the scheme:



The hydrolysis was run in a thermostat, the temperature of which was controlled with an accuracy of ±0.5°. The extent of hydrolysis was determined by the amount of aldehyde groups formed in the hydrolytic cleavage. The iodometric method [1, 2] was used to determine the amount of aldehyde formed. The obtained data are given in Table 1.

SUMMARY

1. The acid hydrolysis of D'-methoxy-D-(hydroxymethyl) diethylene glycol (IV) was studied.
2. D'-Methoxy-D-(hydroxymethyl) diethylene glycol (IV), having a CH₂OH group in the α-position to the acetal linkage, is less stable in acid medium than compounds (II), (III) or (I).
3. The obtained results clearly show that the reduced stability of modified celluloses, containing fragments (II), (III) or (IV), to acid hydrolysis is related to the change in the state of the α-acetal linkage in these fragments.

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A NEW METHOD FOR THE SYNTHESIS OF N-ALKYL-4-PIPERIDONES

E. A. Mistryukov, N. I. Aronova, and V. F. Kucherov

N. D. Zelinskii Institute of Organic Chemistry, Acad. Sci. USSR

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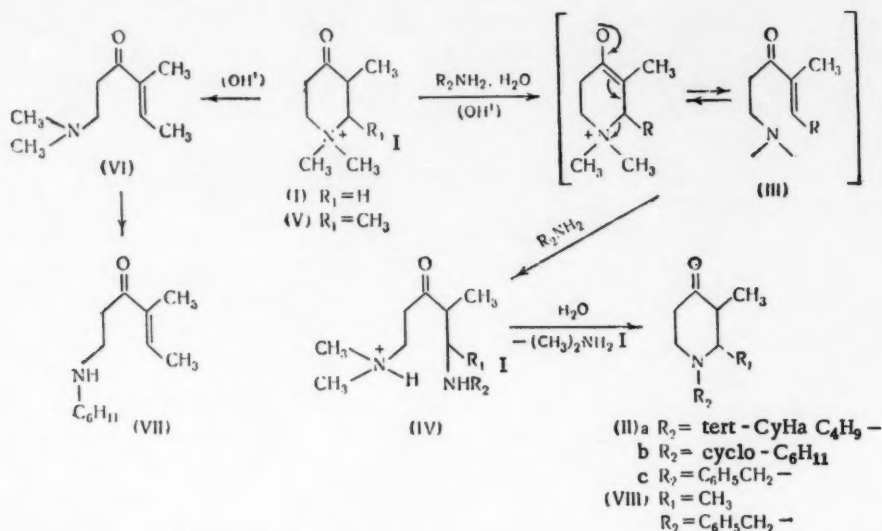
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In a previous paper we described the synthesis of some 4-piperidones with a methyl group or without a substituent on the nitrogen [1]. In order to study the influence of the nature of the substituent on the nitrogen in the esterification of 4-phenyl-4-piperidols [2] it was necessary to synthesize some N-alkyl-4-piperidones with alkyl substituents heavier than methyl. It was found that the readily available N-methyl-4-piperidones [1, 3] could be used as the starting products to obtain the N-alkyl-4-piperidones. The synthesis of the N-alkyl-4-piperidones was accomplished by reacting the methiodides of the 1-methyl-4-piperidones with primary amines (see the analogous reaction of 4-piperidone methiodides with H_2S [4]). The reaction goes with exceeding ease at room temperature and leads to the formation of the corresponding N-alkyl-4-piperidones in excellent yields.

In the case of the substituted 4-piperidones this method proves to be more convenient than the earlier used methods [1, 5]. It is interesting to mention that the methiodide of 1,3-dimethyl-4-piperidone reacts easily even with sterically hindered amines (for example, with *tert*- $C_4H_9NH_2$).



In this way we obtained 3-methyl-4-piperidones with substituents on the nitrogen, namely *tert*-butyl (IIa), cyclohexyl (IIb), and benzyl (IIc). Since we had previously shown [1] that unsaturated aminoketones (type III) are easily cyclized to piperidones using methylamine or ammonia, through the intermediate formation of diaminoketone (IV), then in the present case it is obviously also possible to assume the formation of (IV), either through the addition of the amine to the intermediate unsaturated aminoketone (III) or directly from the methiodide (I) by nucleophilic substitution on the β -carbon atom (see scheme).

From the obtained results it can be seen that an alkyl substituent on C_3 (or C_5) of the piperidine ring exerts little steric effect on the reaction of opening and recyclization of the piperidine ring. Substitution on the β -carbon atom (C_2 or C_6) possesses much greater importance in this respect. Thus, the methiodide of 1, 2, 3-trimethyl-4-piper-

idone gives cyclic products only with unhindered amines (for example, benzylamine). In the case of reaction with hindered amines, for example, tert-butylamine or cyclohexylamine, only opening of the piperidine ring of the methiodide (V) occurs and the reaction products are respectively 3-methyl-6-(dimethylamino)-2-hexen-4-one (VI) or the product of further amino exchange—aminoketone (VII). The noncyclic nature of compound (VII) was shown by the ultraviolet absorption spectrum: aminoketone (VII) absorbs in the region (λ_{\max} 226 m μ , in alcohol) characteristic for α , β -unsaturated ketones. In order to compare the present method of synthesizing N-alkyl-4-piperidones with the McElvain method [5], we attempted to synthesize 1-tert-butyl-3-methyl-4-piperidone (IIa) via the Dieckmann condensation of the corresponding diester. However, it proved that tert-butylamine does not add to methyl methacrylate under the conditions where other amines (see [3]) give the corresponding addition products.

EXPERIMENTAL

1, 3-Dimethyl-4-piperidone methiodide (I). 1, 3-Dimethyl-4-piperidone methiodide was obtained in quantitative yield by treating an acetone solution of 1, 3-dimethyl-4-piperidone with CH_3I . The synthesis of 1, 3-dimethyl-4-piperidone was accomplished either from isopropenylacetylene [1] or by a modification of the Howton method [3]: 326 g of methyl-(2-carbomethoxyethyl) (2'-carbomethoxypropyl) amine was added rapidly to a solution of 36.3 g of metallic sodium in 1200 ml of liquid ammonia; the reaction mixture was stirred for 30 min and then allowed to stand overnight to evaporate the ammonia. The obtained semiliquid mass was treated with 700 ml of ether, and any residual ammonia was removed by heating under reflux (about 1 hr). Then the mixture was acidified with 525 ml of concd. hydrochloric acid in 300 ml of water, the ether was distilled off, and the aqueous solution was boiled until the evolution of CO_2 ceased (1 hr). The excess acid and water were removed by vacuum-distillation, and the dry residue was treated with ether (500 ml), 150 g of solid NaOH, and then gradually with 75 ml of water. From the ether layer we obtained 171.5 g (90%) of 1, 3-dimethyl-4-piperidone with b.p. 62–64° (12 mm); n_D^{20} 1.4572.

Reaction of methiodides of 1-methyl-4-piperidones with primary amines. A mixture of 13.4 g of methiodide (I), 6 ml of cyclohexylamine and 6 ml of water was allowed to stand overnight at room temperature. The free base was isolated from the obtained homogeneous solution by saturation with ammonium sulfate (or potassium carbonate) and extraction with ether. We obtained 7.0 g of 3-methyl-1-cyclohexyl-4-piperidone (IIb); b.p. 106–108° (1 mm); n_D^{21} 1.4907. Found: C 74.24; H 10.80; N 7.50%. $\text{C}_{12}\text{H}_{21}\text{NO}$. Calculated: C 73.79; H 10.84; N 7.17%. Hydrochloride, m.p. 189–190° (from CH_3COOH -ethyl acetate); picrate, m.p. 172–174° (from CH_3COOH). If the crude piperidone (IIb) is purified through the picrate (without distillation), then the yield of the picrate is 66%.

In a similar manner: from 6.5 g of (I) and 6 ml of tert-butylamine in 3 ml of water we obtained 2.3 g of 3-methyl-1-tert-butyl-4-piperidone (IIa), b.p. 104–105° (23 mm); n_D^{20} 1.4558; hydrochloride, m.p. 180–182° (from CH_3COOH -ethyl acetate); picrate, m.p. 182–184° (from CH_3COOH). Found: C 48.21; H 5.48; N 13.74%. $\text{C}_{16}\text{H}_{22}\text{N}_4\text{O}_8$. Calculated: C 48.20; H 5.55; N 14.07%; from 13.4 g of (I) and 5.5 ml of benzylamine in 6 ml of water we obtained 4.13 g of 3-methyl-1-benzyl-4-piperidone (IIc), b.p. 112–117° (1 mm); n_D^{23} 1.5313. Found: C 76.30; H 8.51; N 7.42%. $\text{C}_{13}\text{H}_{17}\text{O}$. Calculated: C 76.81; H 8.43; N 6.89%; picrate, m.p. 160–162°, from alcohol (when purified through the picrate the yield of (IIc) was 66%); from 28.3 g of (V) (m.p. 150–153°, from CH_3COOH) and 10.7 g of benzylamine in 10 ml of water we obtained 11.2 g of 2,3-dimethyl-1-benzyl-4-piperidone, b.p. 124–125° (1 mm); $n_D^{21.5}$ 1.5355; hydrochloride, m.p. 166–167° (from CH_3COOH -ethyl acetate). Found: C 65.99; H 8.12; N 5.54; Cl 13.90%. $\text{C}_{14}\text{H}_{20}\text{NOCl}$. Calculated: C 66.40; H 7.95; N 5.52; Cl 13.97%; from 14.2 g of (V) and 5.3 ml of tert-butylamine in 5 ml of water we obtained 4.7 g of 3-methyl-6-(dimethylamino)-2-hexen-4-one (VI), b.p. 93–95° (25 mm); n_D^{22} 1.4680; λ_{\max} 231 m μ (in alcohol); hydrochloride, m.p. 165–166° (from CH_3COOH -ethyl acetate). Found: C 56.07; H 9.79; Cl 18.60; N 7.99%. $\text{C}_9\text{H}_{18}\text{NOCl}$. Calculated: C 56.38; H 9.46; Cl 18.49; N 7.30% (VI) was also obtained from (V) and aqueous NaOH solution; and from 14.2 g of (V) and 6.5 ml of cyclohexylamine in 5 ml of water we obtained 3.8 g of 3-methyl-6-cyclohexylamino-2-hexen-4-one (VII), b.p. 119–122° (2 mm); n_D^{22} 1.4900; λ_{\max} 226 m μ (in alcohol); picrate, m.p. 172–173.5° (from alcohol). Found: C 51.89; H 6.18; N 12.91%. $\text{C}_{19}\text{H}_{26}\text{N}_4\text{O}_8$. Calculated: C 52.05; H 5.98; N 12.78%.

SUMMARY

A new method, based on the reaction of the methiodides of N-methyl-4-piperidones with primary amines, was proposed for the synthesis of N-alkyl-substituted 4-piperidones.

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LETTERS TO THE EDITOR

REACTION OF ORGANOLITHIUM COMPOUNDS WITH KETOXIDES OF STEROIDS

N. N. Suvorov, L. V. Sokolova, and N. V. Makarov

S. Ordzhonikidze Scientific-Research Chemical-Pharmaceutical

Institute and the Institute of the Chemistry of Natural Products, Acad. Sci. USSR

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In the course of our studies on the synthesis of analogs of dexamethasone we investigated the reaction of methylmagnesium iodide with the ketoxides of steroids [1]. In making a further study of the reactions of alkyl- and aryllithium compounds with the ketoxides of steroids we discovered some interesting cases of the opening of the oxide ring with the formation of 16 β -methyl- and 16 β -phenyl-17 α -hydroxy derivatives, and also their dehydration products.

The reaction of 16 α , 17 α -epoxy-5-pregnen-3 β -ol-20-one 3-acetate 20-ethylene ketal (I) with methyl-lithium, followed by saponification, gave 16 β -methyl-5-pregnen-3 β , 17 α -diol-20-one [m.p. 238–240°; infrared spectrum, in cm^{-1} : 3390, 3333 (OH), 1715 (C=O)] and 16-methyl-5, 16-pregnadien-3 β -ol-20-one [m.p. 196–198°; infrared spectrum, in cm^{-1} : 3401 (OH), 1695 (C=O)].

The reaction of (I) with phenyllithium, after saponification, gave 16 β -phenyl-5-pregnen-3 β , 17 α -diol-20-one [m.p. 272–274°; infrared spectrum, in cm^{-1} : 3401, 3356 (OH), 1692 (C=O), 759, 699 (phenyl)] and 16-phenyl-5, 16-pregnadien-3 β -ol-20-one [m.p. 213–215°; infrared spectrum, in cm^{-1} : 3390 (OH), 1701 (C=O), 757 and 701 (phenyl)].

The structure and configuration of the 16-methyl derivatives was shown by counter syntheses [2]. The structure assigned to the 16-phenyl derivatives was based on the analytical, spectral and potentiometric data, by analogy with the corresponding 16-methyl derivatives. Conclusive proof as to their structure and configuration is being worked upon at the present time.

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RELATIONSHIP BETWEEN RATE CONSTANTS AND BETWEEN
EQUILIBRIUM CONSTANTS OF REACTIONS IN SOLUTION UNDER
PRESSURE

B. S. Él'yanov and M. G. Gonikberg

N. D. Zelinskii Institute of Organic Chemistry, Acad. Sci. USSR

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We found that between the rate constants, and also between the equilibrium constants of reactions in solutions under pressure, there exists a correlation function.

$$\log \left(\frac{K_P}{K_0} \right)_A = \beta \log \left(\frac{K_P}{K_0} \right)_B \quad (1)$$

Here K_P and K_0 are the rate constants (or equilibrium constants) at pressure P and atmospheric pressure, respectively; subscripts A and B relate to the two reactions being compared; β is independent of the pressure. In this connection $\beta = \Delta V_A / \Delta V_B$, where ΔV_A and ΔV_B are the changes in the volume in the formation of the activated complex (or reaction products) from the starting substances in reactions A and B .

Equation (1) was established from an examination of the available data on the equilibrium or kinetics of a large number (over thirty) of reactions under pressure. The indicated correlation bond exists between the equilibrium constants of the dissociation of organic acids and methyl-substituted ammonium bases, the rate constants of the solvolysis of various alkyl halides, the addition of halogen to the double bond, and the isomerization of diethyl maleate. In this connection any pair from the enumerated reactions can be taken as reactions A and B . The various Menshutkin reactions exhibit good correlation between themselves. The found relationship holds in the entire range of pressures studied (up to 3-15 thousand atmospheres).

In its form Equation (1) is analogous to the known Hammett and Einstein-Grunwald equations.

EVENTS

ANNUAL GENERAL MEETING OF THE DEPARTMENT OF CHEMICAL SCIENCES OF THE ACADEMY OF SCIENCES OF THE U.S.S.R. ON THE 31 ST JANUARY, 1961

Translated from *Izvestiya Akademii Nauk SSSR, Otd. Khimicheskikh Nauk*, 1961, No. 5,
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The Annual General Meeting of the Department of Chemical Sciences of the Academy of Sciences of the U.S.S.R. held on the 31st January 1961 in the Institute of Organic Chemistry of the Academy of Sciences of the U.S.S.R., is an important event in the life of the Department. In the report of N. N. Semenov, the academician - secretary of the Department, as well as the co-reports of academician A. P. Vinogradov, deputy academician-secretary of the Department, and academician I. V. Tananaev, member of the Bureau of the Department, the scientific work of the Institutes of the Department of Chemical Sciences and the Branches of the Chemical Institutes carried out in 1960 was summarized proposals for making further progress in improving scientific investigations planned, attention directed towards coordinating work in the most important subjects and methods for avoiding shortcomings were considered.

Having noted that the Party and the Government are paying special attention to the development of chemical science and industry - in particular recalling the historic resolutions of the 1958 May Plenum of the Central Committee of the Communist Party of the Soviet Union - academician N. N. Semenov reported on the main results of the scientific work of the Institutes of the Department on the most important trends in chemistry.

The May Plenum of the Central Committee and the subsequent decisions of the Council of Ministers of the U.S.S.R. and the Central Committee of the Communist Party of the Soviet Union directed the Academy of Sciences to increase its investigations considerably in the field of polymers. At present, the amount of work carried out in the field of polymers, monomers and accelerators is greatest in comparison with other problems of the Department. An increase of work in this region as also proposed, entails a general development in chemical science. It is now no longer possible to confine ourselves merely to an extension of the investigations and a more thorough examination of the problem of polymers and monomers. It is essential without discontinuing efforts in this direction to take steps to extend the work considerably in the other main trends in chemistry also.

A great deal of attention in the report was paid to investigations in the field of naturally and biologically active materials. A new, major problem confronting present day science is the acquisition of knowledge into the nature of the phenomena of life. Today it is possible to pass over to a new stage in our understanding - to a study of the physico-chemical basis of the biochemical processes in which a new science must be applied - biophysical chemistry where physics and physico-chemistry must be brought into close co-operation by biologists and biochemists. On the other hand, it is no less important to study certain materials (albumins, nucleotides, hydrocarbons, antibiotics and so on), the conversion of which constitutes the basis of the biochemical processes. This is the subject of investigation in bio-organic chemistry (the chemistry of natural compounds).

Over the last few years the Department of Chemical Sciences has already taken the first definite steps in both of these general directions. Physico-chemical investigations in the field of the structure of the physico-chemical bases of the biological processes have been developed in the Institute of Chemical Physics and in the Institute of High Molecular Compounds in conjunction with the Laboratories of Radiation Biology in the Institute of Atomic Energy. The recently created Institute of Natural Compounds has turned to work on bio-organic chemistry and has coordinated its activities with the corresponding sections in the Institutes of Elemento-organic Chemical Compounds and Organic Chemistry of the Academy of Sciences of the U.S.S.R. The following most important results were obtained in the division of biophysical chemistry: in the Institute of Chemical Physics the interesting anomaly of magnetic and electrical properties of nucleic acids was discovered; new results in the study of the mechanism of the anti-tumour action

of inhibitors and the mutagenic action of certain active chemical products obtained. In the Institute of High Molecular Weight Compounds the statistical theory of reduplication of DNA (deoxyribonucleic acid) was developed. It was shown that the origin of spontaneous mutations is limited not by thermodynamic but kinetic factors. For the first time electron micro-photographs of ribonucleic acids were obtained. An efficient method was developed and utilized in industry for separating and purifying phenoxymethyl penicillin.

In the division of bio-organic chemistry the most important achievement is the successful development of a new field in the chemistry of natural compounds in the Institute of the same name, i.e. the chemistry of decapeptides—compounds made from alternate residues of hydroxyacids and aminoacids. Many important types of natural materials belong to this class of compound (antibiotics, alkaloids, a number of enzymes, collagen and so on). The Institute of Elementary Organic Compounds, together with the Institute of Evolutionary Physiology obtained interesting data by studying the action of phosphoro-organic compounds on a cholinesterase: a ferment controlling the transmission of a stimulus from the brain and peripheral ganglia to the muscles. Proceeding from certain theoretical conceptions, compounds possessing anti-tumour activity with reduced toxicity have been synthesised and made in quantities sufficient for clinical investigations. An achievement in the region of natural compounds in the Institute of the Chemistry of Natural Compounds was the synthesis of sex hormones — oestrone and new methods of synthesizing vitamin A, developed in the Institute of Organic Chemistry as well as a series of other investigations. But the overall volume of work is definitely not commensurate with the importance appertaining to investigations in this field. The Scientific Council considering the problem of "The chemistry of natural and biologically important compounds" called together to co-ordinate and direct the whole group of investigations in this field must make proposals for a substantial development of work in all the Organo-chemical Institutes of the Department, Branches of the Institutes and Academies of the Soviet Republics.

Considerable attention in the report was given to the development of work in the region of electro-chemistry and the chemistry of semi-conductors. Among the most important questions was the production of new chemical sources of current in the near future characterized by high efficiencies. Having noted the successful work of the Electro-chemical Institutes in this region, academician N. N. Semenov emphasised the necessity for a number of Institutes concerned with organic and physico-chemical subjects to participate in researches on this problem. As well as investigations on the production of a fuel cell, investigations have successfully been started on producing electro-chemical transducers (salt ions) and on electro-chemical kinetics. At the same time, the volume of work carried out on the involved mechanism of electrode processes is still quite inadequate within the departments of the Academy of Sciences.

The volume of work on the chemistry of semi-conductors has been increased to some extent. Certain important practical results have been obtained. In the Institute of General and Inorganic Chemistry ternary solid solutions with valuable thermo-electrochemical properties have been found, the synthesis of boron arsenide — a semi-conductor compound with a high melting point — has been developed. In the Institutes of Electro-chemistry and Physical Chemistry the laws of the interaction of germanium and silicon with oxygen and water vapour have been studied and theories suggested for the stabilization of semi-conductors prepared from these elements. In the Institute of Geochemistry and Analytical Chemistry new methods of analysis of micro-admixtures in a silicon semi-conductor have been developed. Having emphasized the great importance to the natural economy of work in the field of corrosion and having referred to some achievements in this field the reporter at the same time noted that insufficient attention had been paid up to now to the problem of the most expeditious organization of research in this subject.

Work on the synthesis and investigation of the properties of zeolites acquires special significance in the study of the subject of surface phenomena. A substantial contribution in organizing the theoretical and applied investigations of the different institutes and other organizations in this important subject has been made by the Commission actively working on zeolites under the presidency of academician M. M. Dubinin. Real achievements were also noted in work on the compression of powdered materials with the aid of low frequency vibration by vibropressing. A further development of the dislocation theory of brittle fracture has been made and investigations in the field of aerosols and into the properties of thin layers of liquid close to the interfaces of the phases have been carried out.

Considerable attention was paid in the report to problems of using electron computers in chemistry and in particular in the study of the structure of compounds. In the year under review the M-20 computer was constructed which was especially designed for the service of Chemical Institutes. A definite decision to extend the work on the application of quantum chemistry in the theory of structure was taken.

A large proportion of the investigation of the Institute of the Department as before are those in the field of reactivity and chemical kinetics. The most substantial achievements in this field were made in the institutes of Chemical Physics and Elemento-organic Compounds. Over the last period considerable consideration has been given to investigations into the combined reaction in long chain molecules and condensed systems and the problem of intra- and inter-molecular transmission of the excitation energy in the condensed phase. The problem of the further transfer of the charge (electrons and holes) are closely allied to the problem of the transmission of the excitation energy. A typical example is the transfer of an electron by a ferment and the electrical conductivity of organic compounds, in particular polymers, dependent on electrons or holes. The most intensive of these investigations have been carried out in the Institutes of Chemical Physics and Oil-technological synthesis as well as in the Institute of Electro-chemistry. Research into the field of low temperature chemistry which has only been developed over the most recent period is of fundamental importance. In particular, investigations to obtain and study the properties of free radicals and solid bodies at low temperatures and the kinetics of the processes at the temperatures of phase changes are important.

A large section of the report of the academician-secretary of the Department was devoted to researches in the field of polymers and monomers. On the whole, the analysis of the results of the work of the Institutes of the Department for 1960 in this region permitted the conclusion to be drawn that the theoretical level of the investigations is higher and at the same time the work continually becomes more purposeful in the solution of the main problems facing industry. As a shortcoming, it is possible to note the fact that many problems still remain to which the Institutes of the Academy of Sciences pay insufficient attention (modification of industrial polymers, their reprocessing). Investigations on the theory of the resistance to destruction and of the stabilization of polymeric materials are insufficiently developed.

In 1960 there was an extensive development of the work in originating and perfecting new methods in the synthesis of polymers; polyrecombination, polycoordination, stereo-specific polymerization, cyclopolymerization of unconjugated dienes, low temperature catalytic polymerization, onium polymerization and so on. New polymers have been synthesized, including those with a high thermal stability and melting point with a high resistance to dynamic charges, those with interesting magnetic and electrical properties, and polymers possessing catalytic activity. Investigations into the structure and physico-chemical properties of polymers continually rise in importance in connection with the growth in the fields where polymers are used and in the initiation of new methods for their processing. Theoretical investigations on disequilibrium deformation of polymeric materials in the Institute of Elemento-organic Compounds opens the way to construct a resistance theory of polymeric materials and to finding the relation between the structure of the macromolecules and the mechanical properties of the polymers. Interesting results on the influence of the dispersion and preliminary activation of the surface of the filler on the strength and the thermal stability of polymers have been found. Investigations have continued for the introduction of new methods in order to obtain starting products and accelerators for yielding polymers (high rate contact cracking, dimethylating toluene in benzene, the synthesis of formaldehyde, the synthesis of acetic acid and methyl ethyl ketone by liquid-phase oxidation of butane, a new process for obtaining secondary alcohols, the synthesis of cyclodecanol and so on). Investigations into the kinetics and mechanism of polymerization processes have led to the creation of new catalysts and the development of new processes of polymerization. In the review of the year the new methods as well as new polymers developed earlier in the Institutes of the Academy of Sciences (e.g. the polymerization of propylene without solvents, the synthesis of oligomeric polyester acrylates, new silico-organic polymers and materials based on them, block polymers, new methods of obtaining and stabilizing polyformaldehyde and so on) were checked and used under industrial conditions.

In conclusion, academician N. N. Semenov described the course of development of the Institutes of the Department over the last five years. Comparison of the staff of the Institute with the growth in expenditure on scientific-investigational work and on scientific equipment permits the conclusion to be drawn that in this period expenditure on scientific equipment is ahead, which testifies to the increased installation of scientific instruments and equipment. During the same period a preferential growth of craftsmen, production and scientific-technical personnel occurred. All these factors must have a definite effect by increasing the productivity of labour. The main development over the last period was that of the organic and physico-chemical Institutes which had undertaken the solution of the basic problems posed by the resolution of the Central Committee of the Communist Party of the Soviet Union and the Council of Ministers of the U.S.S.R. on polymers. The Inorganic Institutes have developed rather less. But in the near future the Bureau of the Department plan to take measures to strengthen the material resources of these institutes also.

Referring to the further development of the system of Chemical Institutes, academician N. N. Semenov briefly reported on the results of work on the preparation of a twenty year, long term plan of development and the problems

of the existing institutes to train skilled personnel for the recently established institutes in the provinces. The concluding section of the report, devoted to the problems of training skilled personnel, the problem of the interrelation between the older and younger generations of scientists and the question of scientific ethics was listened to with great attention.

A detailed analysis of the main achievements of the Institutes of the Chemical Department in 1960 on problems of using isotopes and radiation in chemistry and geochemistry was given in the co-report of academician A. P. Vinogradov. Investigations over a broad front are carried out in the Institutes of the Department of Chemical Sciences of the Academy of Sciences, U.S.S.R. on the chemistry of transuranium compounds, special consideration is given to investigations of complex compounds of these elements, to the problems of crystallization and cocrystallization and to the problems of extraction and chromatographic separation. Interesting results have been obtained on the effect of radiation on chemical reactions and on the effect of powerful doses of irradiation on the radiation luminescence of vapour, gases and liquids. A number of radiation processes are introduced into industry. As before, the determination of the age of strata by radiochemical methods have been extensively carried out, as a result of which, data on the age of rocks over the whole of Eurasia have been obtained for the first time. Radioactive deposits have been systematically studied and the contamination of soils with radioactive deposits investigated. The growth of C^{14} in the atmosphere during the latter years has been determined by means of analyzing the material of the annual rings of trees. New methods of determination with a dosimeter have been developed. Among the most interesting problems of geochemistry are those of the origin of the materials in the earth's crust and of different rocks. In the Institute of Geochemistry and Analytical Chemistry this problem has been successfully solved by an experimental method. Investigations on explaining the nature of rock formation have been carried out by means of the experimental investigation of hydrothermal processes.

Academician I. V. Tananaev in the co-report presented the main achievements of the Institutes of the Department in the field of inorganic and analytical chemistry. A clear classification of the basic trends in the investigations on inorganic chemistry permitted the reporter in a brief report to describe these trends in an orderly, consecutive manner. In the reporter's opinion inorganic chemistry, due to its great importance in the new developments has, at the present time, entered a period where it is flourishing for the second time. Investigations into the rare elements in particular, have grown. In 1960 the Institutes of the Departments and the Branches of the Institutes investigated the synthesis and studied the properties of practically all the rare elements with the basic aim of obtaining data to solve the problem of their use in new fields and to obtain more refined methods to produce and analyze them. Special attention was paid to the elements with an uncommon valency and to methods for obtaining compounds and elements in a specially pure condition. However the volume of work in these directions can still not be considered as sufficient.

Very great consideration was given to the investigation of complex compounds: synthesis, study of reactivity and in particular the trans-effect. Work on determination of structures has definitely been inadequate. A large volume of work has been carried out in the past in the field of physico-chemical analysis both on the further development of the method and on its application to the investigation of different systems. Of the new important trends the investigation of inorganic polymers is of special importance. Unfortunately, work on this subject is still definitely unsatisfactory. It is necessary to take decisive measures to improve the work both in the sense of material improvement and in the administrative sense. In conclusion, academician I. V. Tananaev proposed a more rational form of organization for the annual general meetings.

A lively discussion took place after the reports in which the following took part: academicians S. I. Vol'kovich, P. A. Rebinder, N. N. Semenov, V. I. Spitsyn, I. V. Tananaev, A. N. Frumkin, M. M. Shemyakin, I. I. Chernyaev; corresponding members K. A. Andrianov, I. P. Alimarin, N. M. Zhavoronkov, I. A. Kazarnovskii and Doctor of Science S. I. Bresler, V. G. Datsko, M. F. Vol'kenshtein, V. P. Markov and others.

Academician A. N. Frumkin discussed the work on the chemistry of semi-conductors, noted the necessity to develop work on the chemistry of metals and on the physico-chemical bases of metallurgical processes in the Institutes of the Department; academician I. I. Chernyaev and Doctor of Chemical Sciences V. P. Markov underlined the need for an urgent solution to the problem of improving the material resources of the Institute of General and Inorganic Chemistry and referred to the perspective of developing work in inorganic chemistry. Academician S. I. Vol'kovich called for help in every possible way to be given to the Institute of General and Inorganic Chemistry to develop its material resources and noted that the theoretical problems of chemical technology in the Institutes of the Department certainly are still not given sufficient attention and urged that the problem of organizing these investi-

gations in the Academy of Sciences should be extensively discussed by an extended session of the Bureau of the Department. The contribution of I. A. Kazarnovskii was also devoted to investigations in the field of inorganic chemistry

Academician V. I. Spitsyn also considered the necessity for a considerable increase in the investigations of the chemistry of radioactive elements and particularly transuranium elements. Corresponding member I. P. Alimarin noted that there are no clear generalizing ideas in the field of inorganic chemistry and there is not sufficient contact between the separate subjects. He attached special importance to the problems of developing the investigations in the field of analytical chemistry, particularly instrumental methods as well as functional analyses of organic compounds; he also noted the unsatisfactory position with skilled analysts and suggested a discussion on the problem of creating large scale laboratories for the analysis of organic compounds.

The deputy academician-secretary of the Department, academician M. M. Shemyakin, described the state of the investigations on the chemistry of natural and biologically active compounds and described the basic problems and the methods to develop this section of science further. He gave special consideration to the problems of training skilled personnel and also to carry out work with modern equipment, without which it is unthinkable to seriously develop this exceptionally important field of science. He urged a general extension of the investigation into this problem in all Organic and Physico-chemical Institutes. The speeches of M. F. Vol'kenshtein and S. E. Bresler were also devoted to investigations in the field of bio-molecular chemistry.

Academician M. M. Shemyakin also turned the attention of the general meeting to the necessity of discovering new ways of holding the monthly sessions of the Department in order to improve this side of the scientific and scientific-organizational activities. Academician P. A. Rebinder underlined the need for broad based investigations in the field of the scientific principles of converting polymers into manufactured articles indicating the great importance of physico-chemical mechanics for the development of this field. The speech of corresponding member of the Academy of Sciences of the U.S.S.R., N. M. Zhavoronkov, was devoted to the problem of training skilled personnel. He said that the Institutes of the Department still do not take the opportunity of using post-graduates, emphasizing that in his opinion the post-graduate was and remains one of the main ways of training qualified staff provided only that intelligence is used when using this system.

The general meeting approved the annual report of the academician-secretary of the Department, academician N. N. Semenov, the co-reports of academician A. P. Vinogradov and I. V. Tananaev and suggested in its future activities to consider the observations and wishes expressed in the discussion. There were also other organizational problems on the agenda of the General Meeting: the election of the Director of the Institute of the Chemistry of Silicates and the award of the academic honorary degree of Doctor to V. V. Serpinskii. The Member of the Academy of Building and Architecture of the U.S.S.R., N. A. Toropov, was elected Director of the Institute of the Chemistry of Silicates.

The General Meeting of the Department of Chemical Sciences adopted, by secret ballot, the resolution, to be referred for ratification by the Presidium of the Academy of Sciences that the award of the honorary degree of Doctor be made to V. V. Serpinskii.

SIGNIFICANCE OF ABBREVIATIONS MOST FREQUENTLY
ENCOUNTERED IN SOVIET PERIODICALS

FIAN	Phys. Inst. Acad. Sci. USSR
GDI	Water Power Inst.
GITI	State Sci.-Tech. Press
GITTL	State Tech. and Theor. Lit. Press
GONTI	State United Sci.-Tech. Press
Gosenergoizdat	State Power Press
Goskhimizdat	State Chem. Press
GOST	All-Union State Standard
GTTI	State Tech. and Theor. Lit. Press
IL	Foreign Lit. Press
ISN (Izd. Sov. Nauk)	Soviet Science Press
Izd. AN SSSR	Acad. Sci. USSR Press
Izd. MGU	Moscow State Univ. Press
LEIIZhT	Leningrad Power Inst. of Railroad Engineering
LET	Leningrad Elec. Engr. School
LETI	Leningrad Electrotechnical Inst.
LETIIZhT	Leningrad Electrical Engineering Research Inst. of Railroad Engr.
Mashgiz	State Sci.-Tech. Press for Machine Construction Lit.
MEP	Ministry of Electrical Industry
MES	Ministry of Electrical Power Plants
MESEP	Ministry of Electrical Power Plants and the Electrical Industry
MGU	Moscow State Univ.
MKhTI	Moscow Inst. Chem. Tech.
MOPI	Moscow Regional Pedagogical Inst.
MSP	Ministry of Industrial Construction
NII ZVUKSZAPIOI	Scientific Research Inst. of Sound Recording
NIKFI	Sci. Inst. of Modern Motion Picture Photography
ONTI	United Sci.-Tech. Press
OTI	Division of Technical Information
OTN	Div. Tech. Sci.
Stroiizdat	Construction Press
TOE	Association of Power Engineers
TsKTI	Central Research Inst. for Boilers and Turbines
TsNIEL	Central Scientific Research Elec. Engr. Lab.
TsNIEL-MES	Central Scientific Research Elec. Engr. Lab. - Ministry of Electric Power Plants
TsVTI	Central Office of Economic Information
UF	Ural Branch
VIESKh	All-Union Inst. of Rural Elec. Power Stations
VNIIM	All-Union Scientific Research Inst. of Metrology
VNIIZhDT	All-Union Scientific Research Inst. of Railroad Engineering
VTI	All-Union Thermotech. Inst.
VZEI	All-Union Power Correspondence Inst.

NOTE: Abbreviations not on this list and not explained in the translation have been transliterated, no further information about their significance being available to us. -Publisher.

Soviet Journals Available in Cover-to-Cover Translation

ABBREVIATION	RUSSIAN TITLE	TITLE OF TRANSLATION	PUBLISHER	TRANSLATION BEGAN Vol. Issue Year
AE	Atomnaya energiya	Soviet Journal of Atomic Energy	Consultants Bureau	1 1 1956
Akust. zh.	Akusticheskii zhurnal	Soviet Physics - Acoustics	American Institute of Physics	1 1 1955
Astr.(on). zh(urn).	Antibiotiki	Antibiotics	Consultants Bureau	4 1 1959
Avto(mat). svarka	Astronomicheskii zhurnal	Soviet Astronomy-AJ	American Institute of Physics	34 1 1957
	Avtomaticheskaya svarka	Automatic Welding	British Welding Research Association (London)	1 1959
	Avtomatika i Telemekhanika	Automation and Remote Control	Instrument Society of America	27 1 1956
	Biofizika	Biophysics	National Institutes of Health*	1 1957
	Biokhimiya	Biochemistry	Consultants Bureau	21 1 1956
Byull. eksp(erim). biol. i med.	Byulleten' eksperimental'noi biologii i meditsiny	Bulletin of Experimental Biology and Medicine	Consultants Bureau	41 1 1959
DAN (SSSR)	Doklady Akademii Nauk SSSR	The translation of this journal is published in sections, as follows:		
Dok(lady) AN SSSR }		Doklady Biochemistry Section	American Institute of Biological Sciences	106 1 1956
		Doklady Biological Sciences Sections (Includes: Anatomy, biophysics, cytology, ecology, embryology, endocrinology, evolutionary morphology, genetics, histology, hydrobiology, microbiology, morphology, parasitology, physiology, zoology sections)	American Institute of Biological Sciences	112 1 1957
		Doklady Botanical Sciences Sections (Includes: Botany, phytopathology, plant anatomy, plant ecology, plant embryology, plant physiology, plant morphology sections)		
		Proceedings of the Academy of Sciences of the USSR, Section: Chemical Technology	Consultants Bureau	106 1 1956
		Proceedings of the Academy of Sciences of the USSR, Section: Chemistry	Consultants Bureau	106 1 1956
		Proceedings of the Academy of Sciences of the USSR, Section: Physical Chemistry	Consultants Bureau	112 1 1957
		Doklady Earth Sciences Sections (Includes: Geochemistry, geology, geophysics, hydrogeology, mineralogy, paleontology, petrography, permafrost sections)	American Geological Institute	124 1 1959
		Proceedings of the Academy of Sciences of the USSR, Section: Geochemistry	Consultants Bureau	106-1 1957-1958
		Proceedings of the Academy of Sciences of the USSR, Section: Geology	Consultants Bureau	123 6 1958
		Doklady Soviet Mathematics	Consultants Bureau	123 6 1958
		Soviet Physics-Doklady (Includes: Aerodynamics, astronomy, crystallography, cybernetics and control theory, electrical engineering, energetics, fluid mechanics, heat engineering, hydraulics, mathematical physics, mechanics, physics, technical physics, theory of elasticity sections)	The American Mathematics Society	131 1 1961
		Proceedings of the Academy of Sciences of the USSR, Applied Physics Sections (does not include mathematical physics or physics sections)		
		Wood Processing Industry	American Institute of Physics	106 1 1956
		Telecommunications		
		Entomological Review	Consultants Bureau	106-1 1956-1957
		Pharmacology and Toxicology	Timber Development Association (London)	9 1959
		Physics of Metals and Metallurgy	Massachusetts Institute of Technology*	1 1957
		Schenov Physiological Journal USSR	American Institute of Biological Sciences	38 1 1959
		Plant Physiology	Consultants Bureau	20 1 1957
		Geochemistry	Acta Metallurgica*	5 1 1957
		Soviet Physics-Solid State	National Institutes of Health*	1 1957
		Measurement Techniques	American Institute of Biological Sciences	4 1 1957
		Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences	The Geochemical Society	1 1958
			American Institute of Physics	1 1959
			Instrument Society of America	1 1959
			Consultants Bureau	1 1952
Derevoobrabat. prom-st'.	Derevoobratvayushchaya promyshlennost'	Wood Processing Industry		
	Elektrsvyaz	Telecommunications		
	Entomologicheskoe obozrenie	Entomological Review		
	Farmakol. (i) toksikol(ogiya)	Pharmacology and Toxicology		
	FMM	Physics of Metals and Metallurgy		
	Fiziol. zhurn. SSSR	Schenov Physiological Journal USSR		
	(im. Sechenova)	Plant Physiology		
	Fiziol(ogiya) rast.	Geochemistry		
	Geokhimiya	Soviet Physics-Solid State		
	Fizika tverdogo tela	Measurement Techniques		
	Izmeritel'naya tekhnika	Bulletin of the Academy of Sciences of the USSR: Division of Chemical Sciences		
	Izv. AN SSSR.			
	Q(td). Kh(im). N(auk)			

continued

Izv. AN SSSR, Otdel. Tekhn. N(auk): Met(ali), i top.	(see Met. i top.)	Bulletin of the Academy of Sciences of the USSR: Physical Series	1	1954
Izv. AN SSSR Ser. fiz(ich).	Izvestiya Akademii Nauk SSSR: fizicheskaya	Bulletin (Izvestiya) of the Academy of Sciences USSR: Geophysics Series	1	1954
Izv. AN SSSR Ser. geofiz.	Izvestiya Akademii Nauk SSSR: Seriya geofizicheskaya	Izvestiya of the Academy of Sciences of the USSR: Geologic Series	1	1958
Izv. AN SSSR Ser. geol.	Izvestiya Akademii Nauk SSSR: Seriya geologicheskaya	Soviet Rubber Technology	18	1959
Kauch. i rez.	Kauchuk i rezina	Kinetics and Catalysis	1	1960
	Kinetika i kataliz	Coke and Chemistry USSR	3	1960
	Koks i khimiya	Colloid Journal	1	1958
Kolloidn. zh(urn).	Kolloidnyi zhurnal	Soviet Physics - Crystallography	14	1952
Metall. i term. obrabot. metal.	Kristallografiya	Metal Science and Heat Treatment of Metals	2	1957
Met. i top.	Metallovedenie i termicheskaya obrabotka metallov	Acta Metallurgica	6	1958
Mikrobiol. OS	Metallurgiya i topliva	Eagle Technical Publications	1	1957
	Mikrobiologiya	American Institute of Biological Sciences	26	1957
	Optika i spektroskopiya	American Institute of Physics	6	1959
	Pochvovedenie	Soviet Soil Science	1	1958
	Priborostroenie	Instrument Construction	1	1958
Pribory i tekhn. eksperimenta)	Pribory i tekhnika eksperimenta	Instruments and Experimental Techniques	1	1959
Prikl. matem. i mekh.	Prikladnaya matematika i mekhanika	Applied Mathematics and Mechanics	1	1957
PTÉ	(see Pribory i tekhn. éks.)	Problems of the North	1	1958
Radiotekh. Radiotekh. i elektronika	Problemy Severa	Radio Engineering	12	1957
	Radiotekhnika	Radio Engineering and Electronics	2	1957
	Stanki i instrument	Machines and Tooling	1	1959
Stek. i keram.	Stal' (in English)	Iron and Steel Institute	1	1959
Svaroch. proizvo	Ssteklo i keramika	Glass and Ceramics	13	1955
Teor. veroyat. i prim.	Svarochnoe proizvodstvo	Welding Production	4	1959
	Teoriya veroyatnostei i ee primeneniye	Theory of Probability and Its Applications	1	1956
	Tsvetnyye metall	Nonferrous Metals	1	1960
Tsvet. Metall	Uspekhi fizicheskikh Nauk	Soviet Physics - Uspekhi (partial translation)	66	1958
UFN	Uspekhi khimii	Russian Chemical Reviews	1	1960
UMN	Uspekhi matematicheskikh nauk	Russian Mathematical Surveys	15	1960
Usp. fiz. nauk	(see UFN)	Russian Review of Biology	48	1959
Usp. khimii(i)	(see UFN)	Russian Engineering Journal	4	1959
Usp. matem. nauk	(see UFN)	Problems of Hematology and Blood	1	1957
Usp. sovr. biol.	Vestnik mashinostroeniya	Problems of Virology	1	1957
Vest. mashinostroeniya	Voprosy gematologii i perelivaniya krovi	Industrial Laboratory	1	1957
Vop. gem. i per. krovi	Voprosy onkologii	Journal of Analytical Chemistry USSR	25	1955
Vop. onk.	Voprosy virusologii	Soviet Physics-JETP	7	1955
Vop. virusol.	Zarodskaya laboratoriya	Russian Journal of Physical Chemistry	28	1955
Zh(ochsk) laboratoriya)	Zhurnal analiticheskoi khimii	Journal of Microbiology, Epidemiology and Immunobiology	7	1959
Zh(ochsk) Zh. anal(it). khimii	Zhurnal eksperimental'noi i teoreticheskoi fiziki	The Russian Journal of Inorganic Chemistry	1	1957
ZhETF	Zhurnal fizicheskoi khimii	Journal of General Chemistry USSR	19	1949
Zh. eksperim. i teor. fiz.	Zhurnal mikrobiologii, epidemiologii i immunobiologii	Journal of Applied Chemistry USSR	23	1950
ZhFZh Zh. fiz. khimii	Zhurnal neorganicheskoi khimii	Journal of Structural Chemistry	1	1960
ZhMEI Zh(urn). mikrobiol. i epidemiol. i immunobiol.	Zhurnal obshchei khimii	Soviet Physics-Technical Physics	26	1956
ZhNH	Zhurnal prikladnoi khimii	Pavlov Journal of Higher Nervous Activity	1	1958
ZhNH	Zhurnal struktural'noi khimii			
ZhNH	Zhurnal tekhnicheskoi fiziki			
ZhNH	Zhurnal vysshei nervnoi deyatel'nosti (vm. I. P. Pavlova)			

*Sponsoring organization. Translation through 1960 issues is a publication of Pergamon Press.

